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Chemical principles of preparation of metal-oxide superconductors

Yu D Tretyakov, E A Goodilin

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Abstract. The review deals with chemical aspects of the problem of preparation of a novel class of advanced materials, viz., high-temperature superconducting cuprates of complex chemical composition and structure. Investigations into these types of superconductors not only made it possible to reveal the ‘composition–treatment–structure–property’ correlations, but also contributed significantly to the development of concepts of chemical interactions in complex oxide systems, high-temperature phase transformations, the nature of peritectic reactions, properties of cuprate melts and structural phase transitions. Particular attention is paid to the analysis of different experimental results obtained in the studies of features of physicochemical processes occurring in complex metal-oxide systems. The bibliography includes 292 references.

I. Introduction

Complex cuprates with a high transition temperature to the superconducting state were discovered more than 12 years ago and called high-temperature superconductors (HTSC).^{1–5} The discovery of HTSC has initiated fundamental investigations into their crystal structure and physicochemical properties as well as the search for possibilities of practical use of these phases.^{6–24}

From the chemical viewpoint, the history of superconductivity is a chain of discoveries of materials with more and more complicated structures and can be considered as specific ‘chemical evolution’ of these materials from simple to complex ones (Fig. 1). This dates back to 1911 when the Dutch physicist H Kamerlingh-Onnes first obtained liquid helium. This breakthrough has made it possible to systematically investigate the properties of materials at temperatures close to absolute zero. Kamerlingh-Onnes had established²⁵ that mercury metal known as a ‘bad metal’ completely loses electrical resistance at 4.2 K. In 1933, Meissner and Oxenfeld showed²⁶ that superconductors (SC) are simultaneously ideal diamagnetics, which means that they completely exclude the magnetic field lines from their own bulk.

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Following the discovery of superconductivity, the common belief was that superconductors would find extensive practical applications. However, this is limited mainly because of a very low transition temperature to the superconducting state (the so-called critical temperature, T_c). In the mid-1980s, it has been possible to raise this temperature^{2, 12, 27, 28} to 23.2 K for Nb₃Ge intermetallic, despite the fact that commonly accepted theories of superconductivity (see, e.g.,²⁶) casted scepticism concerning the possibility of attainment of this high-temperature barrier.

In 1986, Bednorz and Müller²⁹ discovered that ceramics based on copper, lanthanum and barium oxides (La_{2–x}Ba_xCuO₄) can

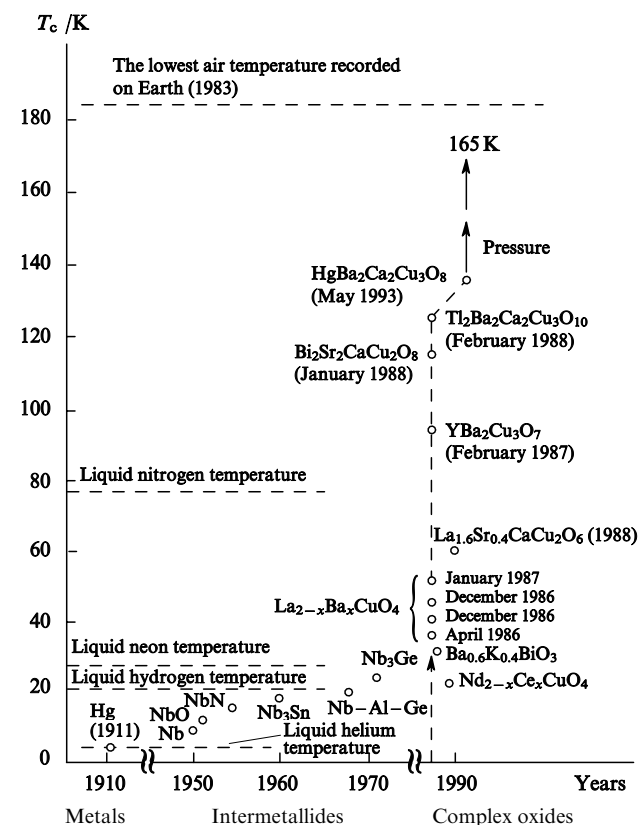


Figure 1. Chronology of discoveries in the field of high-temperature superconductors.

undergo a transition to the superconducting state at 30 K. Mention should be made of studies by Lazarev, Kahan and Shaplygin³⁰ who synthesised complex cuprates of analogous composition in 1978 and of those by a group of researchers from France,³¹ carried out two years later. However, unfortunately, the electrical conductivity of these specimens was measured down to liquid nitrogen temperature (77 K) only, which precluded observation of the effect of superconductivity.

It should be emphasised that high-temperature superconductivity was first observed for an oxide ceramic, which usually possesses dielectric or semiconducting properties, rather than for conventional intermetallides, organic or polymeric structures.²⁶ This destroyed the psychological barrier to the synthesis of HTSC and allowed the synthesis of new generations of metal-oxide superconductors nearly simultaneously and over a short period. The brief history is as follows. In February 1987, using the idea of ‘chemical compression’ for structure modification, Wu *et al.*³² prepared a superconducting ceramic based on barium, yttrium and copper oxides ($\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$) with a critical temperature of 93 K, which is higher than the liquid nitrogen boiling temperature. In January 1988, Maeda *et al.*³³ synthesised a series of compounds with composition $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$. Among them, the phase with $n = 3$ had a T_c of 108 K. A month later, Sheng and Hermann³⁴ prepared a superconductor $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ with $T_c = 125$ K. Finally, in 1993, Antipov, Putilin *et al.*^{35, 36} discovered a series of mercury-containing superconductors with composition $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ ($n = 1-6$). Currently, the $\text{Hg}1223$ -phase of this family has the highest T_c (135 K). It should be noted that at an external pressure of 350×10^3 atm the transition temperature increases to 164 K,^{12, 36} which is only 19 K lower than the lowest temperature ever reached under natural conditions on the Earth. These are the main stages of ‘chemical evolution’ of superconductors from mercury metal (4.2 K) to mercury-containing HTSC (164 K).

Currently, about 50 individual layered superconducting cuprates are known¹⁴ (Table 1). Sometimes, sensational information on the preparation of novel ‘copper-free’ superconductors with T_c above room temperature is reported. ‘Copper-free’ superconductors have been known for some time; however, no high transition temperatures to the superconducting state have yet been observed for these compounds (the highest T_c values for copper-free superconductors were reported for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ and fullerene-based intercalation phase Cs_3C_{60} ³⁷ (see Table 1).

A line of investigations associated with attempts to synthesise ‘ecologically safe’ HTSC free from heavy metals (Hg, Pb, Ba) deserves special mention. Oxycarbonate phases of Ca prepared under high pressure³⁸ can serve as an example of these HTSC.

Thus, most HTSC are oxide phases with very complicated chemical composition. These compounds are extremely sensitive to the conditions for synthesis, heat treatment and operating conditions; they are often called ‘chemical’ superconductors.¹⁴ Numerous studies were devoted to structural,^{12, 17, 18} physical,¹⁹ synthetic^{2-11, 13, 14, 20-22} and technological aspects^{15, 16, 23, 24} of preparation of HTSC materials; however, only very few of them consider all these problems simultaneously. It should be noted that studies of the processes accompanying preparation of HTSC-materials by different methods not only allow the solution of a practically important problem of revealing the ‘composition–treatment–structure–properties’ correlations, but also favours the progress of general chemical ideas of the nature of complex oxide systems, *e.g.*, of the interaction between their components, the effect of mutual rare-earth (RE) element substitution, high-temperature phase relations, the nature of peritectic reactions, the structure and properties of the cuprate melts, oxygen and cation nonstoichiometry of solid phases and structural phase transitions. In this regard, the principles of the synthesis of metal-oxide superconductors are of considerable interest to chemical sciences. This review deals with a systematic consideration of fundamental physicochemical problems related to the preparation of HTSC-materials as well as with analysis of

Table 1. Main types of high-temperature superconductors.

Type of high-temperature superconducting phase	T_c /K	Ref.
$\text{La}_{2-x}\text{M}_x\text{CuO}_4$ (‘La201’-phase, M = Ca, Sr, K, Na, Rb)	35–45	29
$\text{La}_{1.6}\text{Sr}_{0.4}\text{CaCu}_2\text{O}_6$	58	18
$\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ (T-phase, electron superconductor)	23	18
$\text{Nd}_2\text{CuO}_{4-x}\text{F}_x$	27	18
$(\text{Nd}, \text{Sr}, \text{Ce})_2\text{CuO}_4$ (T*-phase)	35	18
$(\text{Y}, \text{R})\text{Ba}_2\text{Cu}_{3+n/2}\text{O}_{7+n/2}$ (‘R123’-phase, R is RE element)	up to 95 ($n = 0$) 60 ($n = 1$) 80 ($n = 2$)	32
$\text{YBa}_2\text{Cu}_3\text{O}_6\text{F}_2$	94	18
$\text{Bi}_2(\text{Ca}, \text{Sr})_{n+1}\text{Cu}_n\text{O}_{2n+4}$ ‘Bi2201’-phase	12 ($n = 1$)	33
‘Bi2212’-phase	85 ($n = 2$)	
‘Bi2223’-phase	108 ($n = 3$)	
$\text{TlBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$ (‘Tl1212’–‘Tl1234’-phases, $n = 1-4$)	125 ($n = 4$)	34
$\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$	95 ($n = 1$) 105 ($n = 2$) 128 ($n = 3$) 115 ($n = 4$)	34
$\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+z}$	98 ($n = 1$) 128 ($n = 2$) 135 ($n = 3$) 125 ($n = 4$) 113 ($n = 5$)	35
$\text{Hg}_2\text{Ba}_2\text{R}_{1-x}\text{Ca}_x\text{Cu}_2\text{O}_8$ (see ^a)	70	35
$\text{Pb}_2\text{Sr}_2\text{R}_{n-1}\text{Cu}_{n+1}\text{O}_{2n+4+z}$ (R is RE element, RE element + Ca)	40–70	2
$\text{CuSr}_2\text{YCu}_2\text{O}_7$	77	12, 14
$\text{AuBa}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{O}_7$ (see ^a)	82	
$\text{Sr}_{0.7}\text{La}_{0.3}\text{CuO}_2$ (see ^a)	40	12, 14
$\text{Sr}_2\text{CuO}_2\text{F}_{2+z}$	47	12, 14
$\text{Sr}_{2-x}\text{K}_x\text{CuO}_2\text{CO}_3$ (see ^a)	23	38
$\text{Sr}_2\text{CaCuO}_{4+z}\text{Cl}_{2-x}$ (see ^a)	80	12, 14
(BO) $\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$ (see ^a)	100	12, 14
(Sr, Ca) $_{n+1}\text{Cu}_n\text{O}_{2n+2}$ (see ^a)	100	12, 14
$(\text{Cu}_{0.5}\text{C}_{0.5})\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_3\text{O}_z$ (see ^a)	124	12, 14
$\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n-2+z}$ (see ^a)	126 ($n = 3$)	12, 14
MC_{60} (fullerides, M = Na, K)	34	37
$\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$	30	2
$\text{Sr}_{0.5}\text{K}_{0.5}\text{BiO}_3$ (see ^a)	13	12, 14
$\text{RNi}_2\text{B}_2\text{C}$	23	12, 14

^a Obtained under pressure.

different experimental results obtained by researchers all over the world.

II. Characteristic features of high-temperature superconductors

1. The crystal structure

An analysis of the available data on the structure and composition of HTSC allows some generalisations to be made.^{14, 36} First, almost all HTSC are complex layered copper-containing oxides whose structure contains oxygen-deficient perovskite-like blocks (Fig. 2). The $(\text{Sr}, \text{Ca})\text{CuO}_2$ phase built of alternating blocks comprising alkaline-earth metal ions sandwiched with planar CuO_2 layers³⁸ is considered as a prototype of the oxide HTSC. It is the CuO_2 layers that are currently considered to be responsible for superconductivity in cuprates. In these layers, the copper atoms form a square network, whereas the oxygen atoms are placed on the lines connecting the copper sites. The electrons

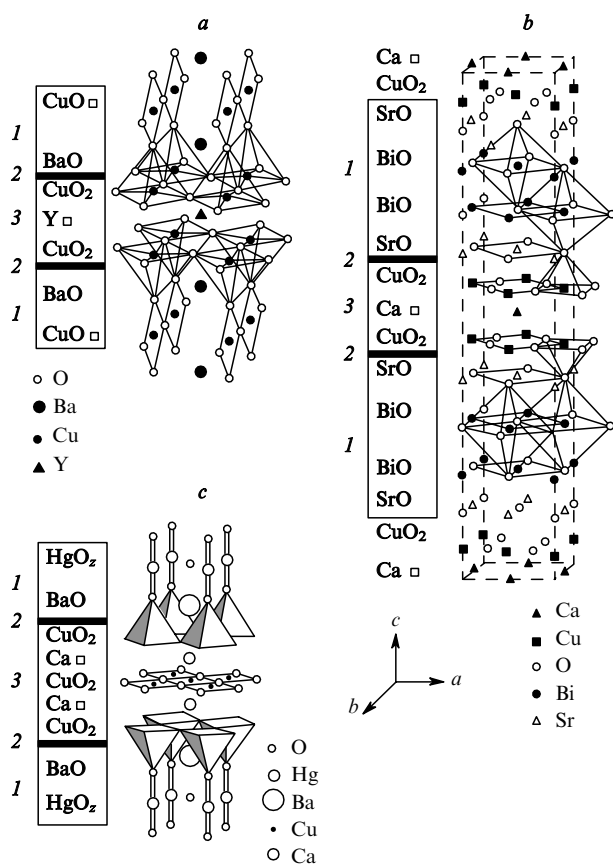


Figure 2. Crystal structures of HTSC YBa₂Cu₃O₇ (a), Bi₂Sr₂CaCu₂O₈ (b), HgBa₂Ca₂Cu₃O_z (c). Dielectric (1) and oxygen-deficient (3) perovskite-like blocks containing superconducting CuO₂ planes (2) are shown.

of copper and oxygen atoms that form Cu–O bonds in such a layer ($3d_{x^2-y^2}$ and $2p_{xy}$ electrons, respectively) are delocalised, which means that they belong not to one but to all of the atoms in the layer. Therefore compounds comprising CuO₂ layers in their structure can possess a metallic-type conductivity. At temperatures below the critical temperature, superconductivity arises

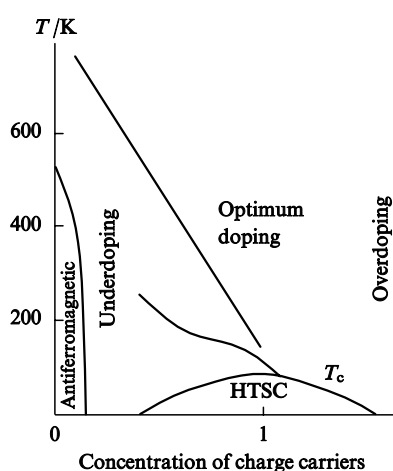


Figure 3. Generalised physical phase diagram of a high-temperature superconductor depending on the relative concentration of charge carriers in the superconducting planes. Mark 1 on the abscissa axis corresponds to the state characterised by the maximum transition temperature to the superconducting state.

upon doping of the CuO₂ layers with an optimum amount of charge carriers (Fig. 3); this occurs upon ordering of oxygen atoms and vacancies after the high-temperature superconducting phase has achieved a certain oxygen stoichiometry, upon hetero-valent doping, upon applying an external pressure, *etc.*^{12, 16, 19}

It was experimentally established that manifestation of superconductivity requires that the formal oxidation state of copper in the CuO₂ layers with collective electrons be somewhat different from +2 and lie within the range from +2.05 to +2.25 for hole superconductors (123-, Bi- and Tl-families) or from +1.8 to +1.9 for electron superconductors^{2, 12} (phases of the Nd₂CuO₄ type). The Cu–O bond length in the layer is yet another important parameter determining the superconducting properties; this must be within the limits 0.190–0.197 nm provided that the distance between the nearest copper atoms lies in the range 0.380–0.394 nm. The copper atoms can also be bonded to the oxygen atoms in neighbouring layers; however, these bonds should be much longer and exceed 0.22 nm. In other words, the structure of superconducting cuprates contains inequivalent Cu–O bonds, *viz.*, strong in-plane bonds in each CuO₂ layer and much weaker bonds directed perpendicular to these layers. As a consequence, such superconductors have a layered structure, whereas the framework-type complex copper oxides (perovskites CuBO₃ with equivalent Cu–O bonds) possess no superconducting properties.

Electrical neutrality of crystals requires the presence of other charge-compensating layers or the presence of dielectric layers between superconducting CuO₂ planes. These interlayers consist of readily polarisable ions (*e.g.*, Ca²⁺, Sr²⁺ and Ba²⁺ ions) which, along with the holes in the CuO₂ layer, can form the Cooper pairs upon transition to the superconducting state.² Most of the known superconductors are built of alternating CuO₂ and BaO, SrO, TlO⁺, BiO⁺, Ca²⁺, Y³⁺, *etc.* layers. Changes in the number of CuO₂ layers in the structure give rise to homologous series of compounds with a similar structure (see Fig. 2). In this case, the crystal structure will be stable if each constituent layer is commensurate with the layers lying above and below a given layer.

This analysis of the genesis of the structure of different HTSC families is not only useful for finding a general approach to the description of the phenomenon of high-temperature superconductivity, but also favours a targeted search for and chemical design of novel superconductors.

2. Physical properties

In most cases, the practical applications of superconductors are associated with their capability to resist in the superconducting state the destructive action of a current density of $\sim 10^5$ A cm⁻² in magnetic fields from 2 to 10 T, while the first (ceramic) specimens of superconducting cuprates were characterised by more than modest critical current density^{8, 10} of ~ 1 –100 A cm⁻² (Fig. 4).

Currently, synthesis of superconducting phases with the desired crystal structure and T_c above the liquid nitrogen temperature can be accomplished without difficulty. However, the attainment of high values for other important parameters, *e.g.*, the critical current density J_c and its stability in an external magnetic field, faces great difficulties for a number of reasons. For instance, evolution from metallic to ceramic superconductors results in an increase in T_c and, at the same time, in a dramatic decrease in the coherence lengths of oxide superconductors¹⁹ compared to those of low-temperature intermetallide superconductors (0.2 nm and ~ 2 nm, respectively). The fundamental physical parameters of high-temperature superconducting YBa₂Cu₃O_z phase are listed in Table 2 as examples. As a consequence, the grain boundary thickness in polycrystalline metallic superconductors is commensurate with the coherence length, which favours the appearance of efficient pinning centres and an increase in the critical current. On the contrary, the superconduction current in oxide superconductors is to a great extent limited by processes occurring at grain boundaries; this is

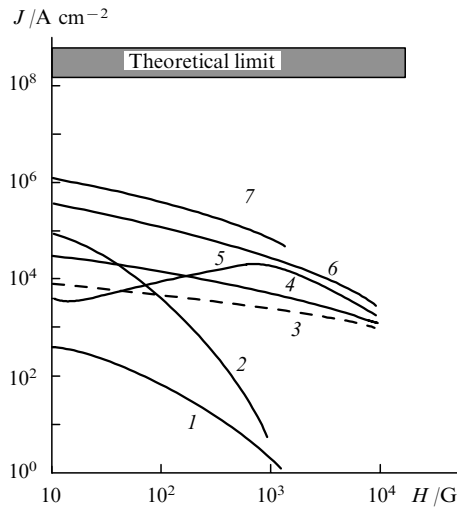


Figure 4. Dependence of the stability of the critical current density on the external magnetic field at 77 K for different classes of HTSC materials; (1) sintered ceramics; (2) Bi2212 tapes; (3) single crystals; bulk melt-solidified ceramics: (4) Y123; (5) Nd123; (6) Y123 doped with ^{235}U and irradiated with slow neutrons and (7) thin films.

the reason why the demands imposed on the state of the intercrystallite boundary are so severe.^{9–11} The situation is complicated by the fact that, because of the specific layered structure, almost all high-temperature superconducting phases possess a very high crystallographic anisotropy of physical properties, which requires texturing of the polycrystalline material.¹¹

Additionally, HTSC are type II superconductors. In an external magnetic field, they can exist in the mixed state where the magnetic flux partly penetrates the superconductor in the form of the so-called Abrikosov fluxoids.¹⁹ As a rule, the vortex lattice thus formed becomes more stable if extra pinning centres are generated. It is assumed that each pinning centre is a distortion of the superconductor structure (a structural defect), the size of which is comparable with the coherence length.^{11, 19} Generation of efficient pinning centres in high-temperature superconducting

materials is necessary since the practical use of HTSC in the heavy-current devices requires not only high critical current densities, but also enhanced current stability in external magnetic fields.

3. Chemical behaviour

The preparation of modern high-temperature superconducting materials encounters considerable difficulties due to the complexity of their chemical composition and structure (and, as a consequence, to the thermal and chemical instability).²⁷ The fact that solid-phase (ceramic) synthesis of superconducting cuprates is simple and rapid, as well as giving a first preparation of defect-free (according to visual inspection) as-grown small single crystals only gave the deceptive impression that most problems had been left behind. However, conventional methods of solid-phase synthesis of HTSC appeared to be inefficient for the preparation of materials with the desired properties. Because of this, the development of melt solidification methods^{6–11} has begun. These methods are based on melt crystallisation under controlled conditions, which allows a complex treatment of the real structure of the material. It should be noted that almost all HTSC are characterised by incongruent melting and their melts are multi-component heterogeneous (containing both gaseous and solid phase along with the melt) open systems (participating in oxygen exchange with environmental gases), shifted apart from thermodynamic equilibria.

This can be exemplified in the family of high-temperature superconductors, *viz.*, $\text{RBa}_2\text{Cu}_3\text{O}_x$ phases (R123-phases, R is a RE element) studied in most detail. These complex cuprates are composed of such chemically different components as stoichiometric (with respect to oxygen) high-melting oxides of alkaline-earth and RE elements (BaO and R_2O_3) and a low-melting 'acidic' oxide of a transition metal (copper) in different oxidation states. As a result, the problem arises of oxygen nonstoichiometry, which requires consideration of the phase diagrams for quaternary $\text{R}_2\text{O}_3\text{--BaO--CuO}_n\text{--O}_2$ systems with complicated 'pO₂–temperature–composition' relations (especially in the region where the solid and liquid phases coexist) instead of conventional isothermal $\text{R}_2\text{O}_3\text{--BaO--CuO}$ phase diagrams. In addition, RE-element-for-barium substitution solid solutions can be formed because of rather large ionic radii of 'light' RE elements (La, Pr, Nd, Sm, Eu, Gd); their equilibrium composition in the supersolidus region is determined by the composition of the melt equilibrated with the solid solution.⁸ This complicates further the general pattern of phase relations and makes optimisation of the processes of preparation of high-temperature superconducting materials more difficult.

Thus, the main problems are (i) the formation of nonstoichiometric (with respect to both oxygen and cations) solid solutions with a preset composition, the degree of chemical homogeneity (*i.e.*, with a particular macroscopic and microscopic distribution of the solution components) and (ii) targeted formation of a real structure of high-temperature superconducting material which provides the desired set of 'structurally sensitive' properties. Accompanying (and sometimes no less important) problems are the investigation of the stability of this type of solid solution including the study of metastable states of high-temperature superconducting phases and their low-temperature decomposition,^{7, 8} the study of equilibrium phase diagrams of high-temperature superconducting systems,^{8–11} the effects of their prehistory and topochemical memory,^{39, 40} chemical degradation of HTSC,^{2, 22} procedures for the preparation of superconducting composites,^{2, 6, 13, 15, 16, 23, 24} *etc.*

III. Phase diagrams of high-temperature superconductors

Phase diagrams reflect the phase states and phase relations depending on the temperature, pressure and the concentrations of the components in the systems. Therefore, it is reasonable to begin the analysis of efficient methods for the synthesis of metal-

Table 2. The Ginsburg–Landau parameters of the HTSC $\text{YBa}_2\text{Cu}_3\text{O}_x$ -phases ($T_c = 92$ K).¹⁹

Parameter	Calculation	Experiment	BCS ^a
Anisotropy			
$k_{ ab}$	74	—	—
$k_{\perp ab}$	2750	—	—
k_{av}	245	—	150
Coherence length /nm			
$\xi_{ ab}$	1.2	—	—
$\xi_{\perp ab}$	0.2	0.3	—
ξ_{av}	0.7	0.7	0.9
Landau's penetration depth /nm			
$\lambda_{ ab}$	89	—	—
$\lambda_{\perp ab}$	550	—	—
λ_{av}	160	140	134
Critical magnetic field /mT			
$H_{c1}(\perp ab)$	90	95–110	—
$H_{c1}(\parallel ab)$	21	24	—
$H_{c1}(0)$	1.0	—	1.1
$-\text{d}H_{c1}/\text{d}T/\text{mT K}^{-1}$	22	—	19
$-(\text{d}H_{c2}/\text{d}T)_{av}/\text{T K}^{-1}$	8	—	4.6
$\Delta C/\gamma T_c$	2.21	—	2.23
$(\gamma = 18.2 \text{ mJ mol}^{-1} \text{ K}^{-2})$			

^a The Bardeen–Cooper–Schrieffer model.

oxide superconductors with the most comprehensively and reliably studied $R-Ba-Cu-O$ systems in order to demonstrate general principles of the use of phase diagrams for the preparation of high-temperature superconducting materials. Investigations into the phase diagrams of a promising and technologically important $Nd-Ba-Cu-O$ system,^{7,8,16} which exhibits the salient features of the phase diagrams of cuprate superconductors in the supersolidus region seem to be the most interesting.

1. Subsolidus phase relations

a. Geometrical factors and phase stability

Most superconducting compounds are thermodynamically stable only in narrow ranges of temperature and partial pressure of oxygen; many of them are metastable under storage and operating conditions. Therefore, one can hardly find high-temperature superconductors (especially, among the last-generation materials) free from dopants stabilising their structure. As a rule, superconducting complex oxides are solid solutions with fairly wide homogeneity regions and comprise several elements with close crystallochemical characteristics. Internal structural strain is naturally relieved due to the difference in the ionic radii of the constituent elements.^{2,17,18,36} ‘Chemical’ deformation of the crystal structure of superconductors due to doping, as well as that caused by external pressure, can lead to essential changes in the superconductivity parameters due to changes in the distances between the superconducting planes and dielectric blocks and/or to the charge redistribution between them.^{41–45} Because of this, the consideration of geometrical factors seems to be of great importance. The following types of substitution affecting the properties of high-temperature superconducting phases and the phase relations in high-temperature superconducting systems can be distinguished, (i) variation of RE elements (R) in $R-Ba-Cu-O$ systems; (ii) Bi/Pb substitution in bismuth-containing HTSC; (iii) Hg/Pb, Hg/Re and Ba/Sr substitutions in mercury-containing HTSC;^{36,46,47} (iv) substitutions of alkaline-earth cations in binary and ternary cuprates; and (v) fluorination of $RBa_2Cu_3O_{z-j}F_j$ phases.⁴⁸

The simplest method for assessing the stability of oxide superconductors is based on the well-known Goldschmidt criterion for tolerance, according to which a perovskite-like structure $ACuO_3$ is stable² if $0.8 < t < 1$, where

$$t = \frac{r_A + r_O}{\sqrt{2}(r_{Cu} + r_O)}$$

and r are the ionic radii of the elements constituting the crystal lattice. The use of different REE is the most prominent example and important method of chemical modification of HTSC, since the radii of R^{3+} cations with close chemical properties monotonically decrease due to the effect of lanthanide contraction. Along with the differences in the magnetic moments of R^{3+} ions, energies of their stabilisation by the ligand crystal field and possible oxidation states (+4, +3 or +2), the above-mentioned geometrical factor provides an additional degree of freedom in the synthesis of superconducting phases.

Currently, almost all RE analogues of $YBa_2Cu_3O_z$ have been synthesised by isomorphous substitution of yttrium.^{7,12,18,22} As has been mentioned above, the unit cell of the $RBa_2Cu_3O_z$ phase can be represented as three perovskite-like blocks containing barium or yttrium ions at the centre (see Fig. 2). Phases of the $RBa_2Cu_3O_z$ type are characterised by two oppositely directed effects,⁴⁹ viz., by structure stabilisation towards simple oxides due to the coordination of barium ions and the formation of BaO_{10} polyhedra and by structure destabilisation owing to the formation of RO_8 , CuO_4 and CuO_5 polyhedra. Small ionic radii (R^{3+}) of ‘heavy’ REE and yttrium result in the ‘repulsion’ of oxygen ions in a smaller polyhedron (RO_8) and generation of steric hindrances. Almost no structure destabilisation effect is observed for ‘light’ REE with the largest ionic radii ($Nd-Gd$) in the case of

isomorphous isovalent replacement of the yttrium ion by its RE analogues.

The oxygen content, which affects both the concentration of the charge (hole) carriers in superconducting CuO_2 planes and the average $Cu-O$ bond length, is the second factor influencing the stability of high-temperature superconducting phases with the $YBa_2Cu_3O_z$ structure. It is noteworthy that the estimates of both the lower and upper limits of thermal stability of the phases under consideration^{50,51} suggest that tetragonal non-superconducting modifications ($RBa_2Cu_3O_6$) are more stable than the orthorhombic superconducting phases characterised by higher content of oxygen ($RBa_2Cu_3O_7$) and ‘holes’. The decrease in the thermal stability of solid solutions with partial substitution of REE cations for barium cations in the structure, in which the average oxidation state of copper increases in parallel to the increase in the degree of heterovalent substitution, is an additional confirmation of this hypothesis.

The two above-mentioned structure destabilisation factors should also be taken into account when analysing the ‘geometrical’ stability of bismuth-containing superconducting cuprates (see Fig. 2b).⁵² In these systems, almost all the most important phases are non-stoichiometric compounds with respect to all of the components. According to the data reported,^{53–55} the superconducting phase of the $Bi_2Sr_2CaCu_2O_z$ type (2212-phase) is Bi-excessive and (Ca + Sr)-deficient and the ‘ideal’ 2:2:1:2 composition seems not to be a single phase. The reasons for the existence of such a wide homogeneity region can be⁵³ (i) isomorphous substitution of calcium ions for strontium ions⁵⁶ and, to a lesser extent, partial hetero-valent substitution of strontium and calcium ions for bismuth ions; (ii) the formation of intergrowth structures with higher and lower homologues containing different amounts of calcium and copper and (iii) exchange between the crystallographic positions of bismuth and copper atoms due to the packing faults of the layered structure. Compared to $RBa_2Cu_3O_z$ phases in which the dielectric ‘barium’ block exhibits a fairly high ‘geometrical’ stability, the dielectric Bi_2O_2 blocks can additionally contribute to the structure destabilisation.

A formula was proposed⁵² for assessing the relative stabilisation of bismuth-containing HTSC with extra oxygen and with lead ions which replace bismuth ions in the structure

$$\frac{t}{t_0} = 1 + \left(\frac{\alpha}{y_0} + \frac{2\gamma}{nz_0} \right) \delta + \left(\frac{\beta}{y_0} + \frac{\gamma}{nz_0} \right) x.$$

Here t is the parameter of the criterion for ‘geometrical’ stability of a bismuth-containing high-temperature superconducting phase doped with lead and containing extra oxygen, t_0 is the analogous parameter for a ‘pure’ bismuth-containing high-temperature superconducting phase, α , β and γ are constants, n is the number of superconducting CuO_2 planes, δ is the amount of extra oxygen and x is the degree of lead-for-bismuth substitution.

It was assumed⁵² that the length of the ‘in-plane’ Bi–O bond is determined by the relationship

$$y = y_0 + \alpha\delta + \beta x,$$

whereas the $Cu-O(2)$ bond length is determined by the relationship

$$z = z_0 - \gamma h,$$

where h is the concentration of ‘holes’. According to calculations, the highest stabilisation of superconducting structure (especially at large n , i.e., for higher members of the homologous series) can be achieved, as in the case of 123-phases, if the internal structural strain is relieved by doping the oxide matrix with cations with large ionic radii (in this case, by doping with lead ions in the Bi_2O_2 block).

The virtually planar structure of the CuO_2 layers^{35,36} is a possible reason for the record transition temperatures to the

superconducting state for mercury-containing HTSC. Therefore the geometrical factors can directly affect fundamental superconducting characteristics of a system. Schematically, the structure of $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ phases can be represented as $(\text{HgO}_\delta)(\text{BaO})(\text{CuO}_2) \cdot [(\text{Ca})(\text{CuO}_2)]_{n-1}(\text{BaO})(\text{HgO}_\delta)$ layers stacked along the c axis of the unit cell.³⁶ These compounds have primitive tetragonal unit cells in which the parameter c increases as the thickness n of the perovskite fragment $c(\text{\AA}) = 9.5 + 3.2(n-1)$ increases.

The coordination of the copper atoms in CuO_2 layers varies from octahedral in the Hg1201-structure to tetragonal-pyramidal in the Hg1212-phase and to the square and tetragonal-pyramidal in the Hg1223-phase as the thickness of the perovskite fragment increases. The octahedra and tetragonal pyramids are appreciably elongated along the c axis due to Jahn–Teller distortion. Long Cu–O bonds between the copper atom and the axial oxygen atom and, correspondingly, a very weak interaction between these atoms in the coordination polyhedra of copper are the salient features of the structure of mercury-containing HTSC. On the other hand, a successive increase in the thickness of perovskite fragments owing to the incorporation of additional CaCuO_2 blocks results in compression of interatomic planar Cu–O distances in the structures of higher homologues. This can be interpreted as anisotropic ‘chemical’ compression and results in the distortion of the CuO_2 layers with an increase in n and in corrugation of their planarity. As a consequence, the highest homologues are characterised by lower transition temperatures to the superconducting state. This effect of anisotropic chemical pressure is several times stronger than that caused by external isotropic pressure.⁵⁷ Therefore, it can be suggested that the use of non-traditional methods of chemical synthesis (*e.g.*, layer-by-layer epitaxial deposition of thin films on the substrates with specially chosen parameters) rather than conventional isovalent cation substitution resulting in isotropic compression of the structure will be the most promising way for structure modification to achieve higher T_c . The use of these substrates can result in anisotropic deformation of the crystal lattice of a high-temperature superconducting phase.⁵⁸

A limited set of cations which constitute high-temperature superconducting phases along with copper and oxygen atoms is a factor that restricts the search for new superconducting materials. As has been mentioned above, this is associated with the necessity of meeting the conditions of commensurability of interatomic distances and electrical neutrality. The possibility of varying the composition of the anionic sublattice appreciably extends the area of search; this has been exemplified successfully with F^- anions, the crystalchemical characteristics of which are close to those of O^{2-} ions.⁴⁸ Incorporation of fluorine into the structure of the non-superconducting oxide $\text{YBa}_2\text{Cu}_3\text{O}_6$ results in its oxidation with the formation of the $\text{YBa}_2\text{Cu}_3\text{O}_6\text{F}_2$ phase with $T_c = 94$ K. In this case, several copper atoms in the structure have an octahedral environment consisting of four fluorine atoms and two axial oxygen atoms. In such a structure, the symmetry of the high-temperature superconducting phase remains tetragonal after oxidation because of the absence of ordering of the anions and oxygen vacancies in the CuO_2 plane of the dielectric (‘barium’) perovskite-like block. An increase in the coordination number of copper atoms is accompanied by strong Jahn–Teller distortion of the $\text{Cu}(\text{O},\text{F})_6$ octahedra, which is responsible for the appreciably larger parameter c of the fluorinated phase compared with that of its oxide analogue (12.8–13.2 vs. 11.8 Å, respectively).

Geometrical factors also affect the stability of the most important non-superconducting phases in the systems under consideration, in particular, that of binary and ternary cuprates containing RE and alkaline-earth elements.^{59–64} For instance, the formation of ‘blue’ phases of the $\text{Y}_2\text{Cu}_2\text{O}_5$ type (the 202-phase) is characteristic of REE of the yttrium group, whereas ‘light’ REE with large ionic radii form phases of the La_2CuO_4 type (the 201-phase).⁵⁹ ‘Green’ R_2BaCuO_5 phases with the framework structure, obtained for almost all REE, are stable in air up to

1250 °C.^{8,17,59,61} ‘Light’ REE with large ionic radii form the ‘422-phases’ with composition $\text{R}_{4-2x}\text{Ba}_{2+2x}\text{Cu}_{2-x}\text{O}_{10-2x}$ ($\text{R} = \text{La}, \text{Nd}$),^{59,61} which is associated with the formation of brown solid solutions rather than green substances at $0.15 \leq x \leq 0.25$ for $\text{R} = \text{La}$ and at $0 \leq x \leq 0.1$ for $\text{R} = \text{Nd}$, the latter being characteristic of the Y_2BaCuO_5 phase.

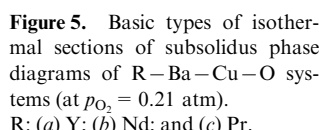
The changes in the ionic radii of alkaline-earth elements (Ba, Sr, Ca), whose binary cuprates play a special role in high-temperature superconducting systems, also result in essential changes in the phase diagrams.^{60,61,63} It is suggested that two cuprates with Ba : Cu ratios of 2 : 3 and 3 : 5 exist in the Cu-rich region of the phase diagram of the BaO–CuO system (see S.1).[†] Like BaCuO_2 , these cuprates can formally be considered as compounds belonging to the BaO–CuO–‘ Cu_2O_3 ’ system since they have a rather wide oxygen homogeneity region (see S.2). An increase in the temperature and a decrease in the p_{O_2} results in decomposition of $\text{Ba}_2\text{Cu}_3\text{O}_5$ and $\text{Ba}_3\text{Cu}_5\text{O}_8$ with the liberation of CuO and the formation of BaCuO_2 , which is stable in air up to ~ 1015 °C (at this temperature, the compound melts with the evolution of oxygen).

Barium cuprate Ba_2CuO_3 , which is thermally stable at high p_{O_2} , is found in the Ba-rich region of the phase diagram of the BaO–CuO system. Cuprite BaCu_2O_2 containing monovalent copper is the only phase stable at reduced partial pressure of oxygen and/or at high temperatures. The phase relations in the Ca–Cu–O system exhibit some specific features as compared with Sr–Cu–O and Ba–Cu–O systems, which is probably due to the impossibility of calcium ion, which has the smallest ionic radius among alkaline-earth metal cations, to stabilise Cu^I and Cu^{III} .^{22,23,61} No stoichiometric quaternary compounds were found in the Sr–Ca–Cu–O system, whereas the stability of solid solutions of mixed strontium and calcium cuprates is determined by the temperature and partial pressure of oxygen, as in the case of the Ba–Cu–O system. At high p_{O_2} and moderate temperatures, the cuprate $\text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}\text{O}_{41+\delta}$ is stable. An increase in temperature and/or a decrease in p_{O_2} results in sequential formation of the cuprate phases $\text{Sr}_{1-x}\text{Ca}_x\text{CuO}_2$ (1 : 1) and $\text{Sr}_{2-x}\text{Ca}_x\text{CuO}_3$ (2 : 1) and the cuprite $\text{Sr}_{1-x}\text{Ca}_x\text{Cu}_2\text{O}_{2+\delta}$ (1 : 2).

Perhaps the most spectacular example of changes in the phase relations caused by geometrical factors is represented by R–Ba–Cu–O systems. There are three main types of quaternary isothermal cuts of the subsolidus phase diagrams of these systems.⁶² The simplest type (Fig. 5a) is characterised by the presence of a ‘point’ $\text{RBa}_2\text{Cu}_3\text{O}_z$ phase formed by ‘heavy’ REE of the yttrium subgroup with the smallest ionic radii (Y, Dy, Ho, Er, Tm, Yb, and Lu), though the phase relations for Yb and Lu can have some peculiarities due to relative instability of the 123-phases.⁶³ Solid solutions of the $\text{R}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ type (Fig. 5b) are formed in systems with ‘light’ REE with large ionic radii (La, Nd, Sm, Eu, and Gd). In these systems, the variation of the composition of non-superconducting (secondary) phases, which play a significant role in the processes of peritectic melting and crystallisation, and of the equilibrium tie-triangles depends on the ionic radii and nature of the REE. The third type of phase relations (Fig. 5c), which differs from the two preceding cases in the absence of the phase of the 211/422-type,^{61–63} is characteristic of the Pr–Ba–Cu–O system. In the Pr- and Ba-rich region, the Pr_{123}ss phase is in equilibrium with the $\text{Pr}(\text{IV})$ -containing phase of the PrBaO_3 type. No compounds with the 1 : 2 : 3 stoichiometric composition are formed in systems containing Ce and Tb for which the most characteristic oxidation state is +4.⁶¹

Systems $\text{Bi}(\text{Pb})\text{–Sr–Ca–Cu–O}$, $\text{Tl–Ba}(\text{Sr})\text{–Ca–Cu–O}$ and $\text{Hg}(\text{Re},\text{Pb})\text{–Ba}(\text{Sr})\text{–Ca–Cu–O}$ are quinary or even septenary, therefore their phase diagrams are extremely com-

[†] The letter S denotes Supplement which contains notes added in proof (the results reported when preparation of the manuscript was completed as well as the results obtained in recent studies and accepted for publication elsewhere).



The volatility of metal-containing components further complicates the problem of stabilisation of these structurally complex superconducting phases. If the doping of phases in the Bi—Sr—Ca—Cu—O system with lead oxides can be considered mostly as a convenient procedure for enhancing the formation dynamics of higher homologues of metal-oxide SC,^{53, 69} the search for possibilities of stabilisation of the structure of mercury-containing HTSC (*e.g.*, by doping with rhenium,^{36, 68} lead and/or strontium^{46, 47, 65} compounds) is of prime importance.

In early studies, metastability of superconducting phases was often considered as the condition for the existence of high-temperature superconductivity;^{1,2} however, the results of modern investigations do not confirm this assumption. Nevertheless, the problem of chemical metastability of high-temperature superconducting phases still remains topical, since this can have both negative and positive consequences from the practical viewpoint. Generally, this is associated with the analysis of the evolution of states of a supersaturated (with respect to one or several components) solid solution under given conditions.

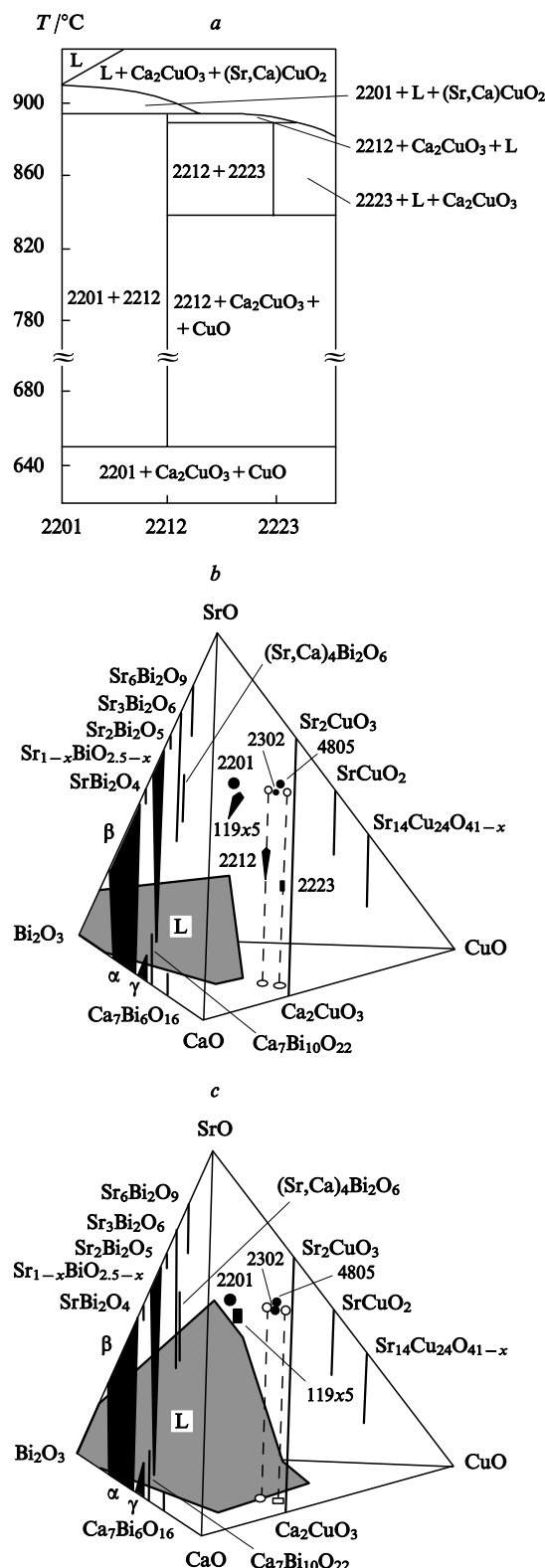


Figure 6. Types of phase diagrams of the Bi–Sr–Ca–Cu–O system (at $p_{\text{O}_2} = 0.21$ atm); (a) polythermal section along $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ – $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$; phase relations in a quasi-quaternary system Bi_2O_3 – CaO – SrO – CuO at 850 (b) and 910 °C (c).

Phase relations in systems containing 'light' REE (La, Pr, Nd, Sm, Eu and Gd) are very complicated because of the formation of solid solutions of the $\text{LR}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ type; difficulties in synthesising several phases of the stoichiometric 123-composi-

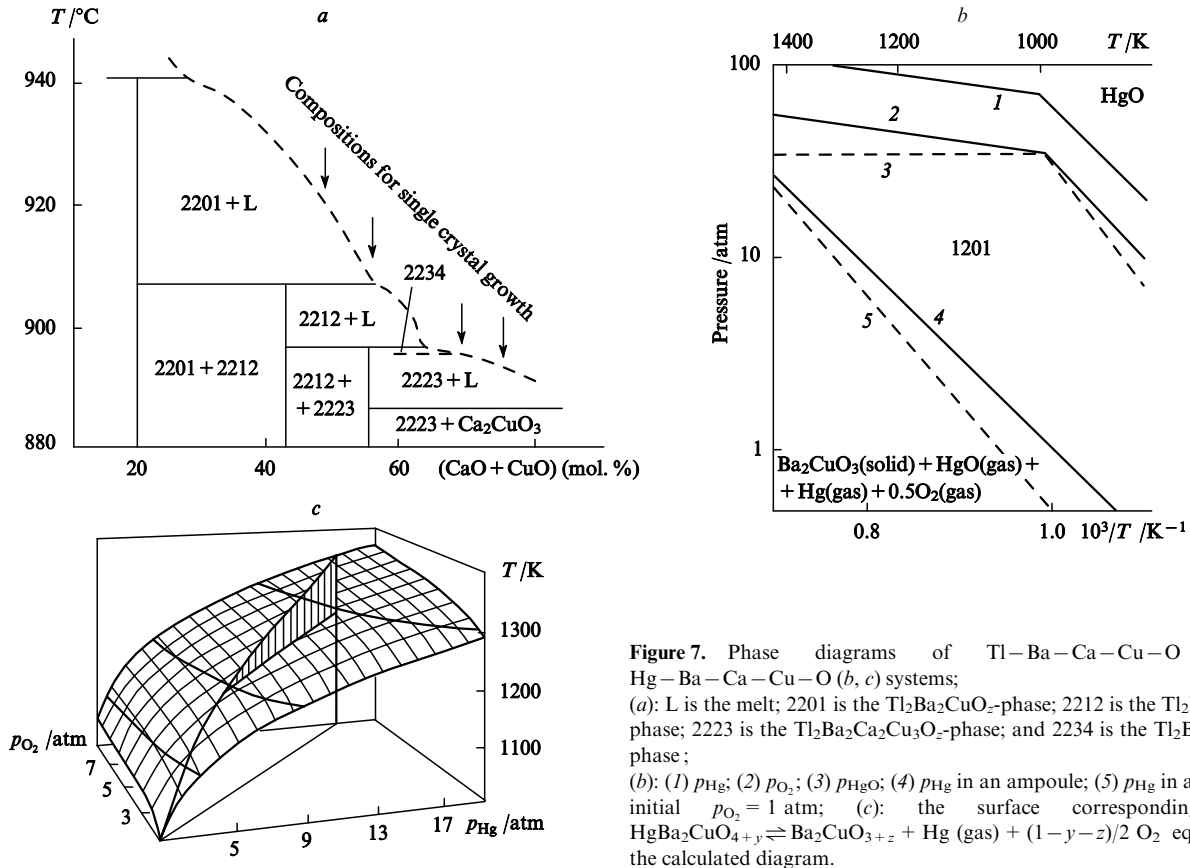


Figure 7. Phase diagrams of Tl–Ba–Ca–Cu–O (a) and Hg–Ba–Ca–Cu–O (b, c) systems; (a): L is the melt; 2201 is the $\text{Tl}_2\text{Ba}_2\text{CuO}_x$ -phase; 2212 is the $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_x$ -phase; 2223 is the $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ -phase; and 2234 is the $\text{Tl}_2\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_x$ -phase; (b): (1) p_{Hg} ; (2) p_{O_2} ; (3) p_{HgO} ; (4) p_{Hg} in an ampoule; (5) p_{Hg} in an ampoule at initial $p_{\text{O}_2} = 1$ atm; (c): the surface corresponding to the $\text{HgBa}_2\text{CuO}_{4+y} \rightleftharpoons \text{Ba}_2\text{CuO}_{3+z} + \text{Hg}(\text{gas}) + (1-y-z)/2 \text{O}_2$ equilibrium on the calculated diagram.

tion containing REE (La, Nd and Sm) have also been reported.^{7, 8, 70–79} It was shown that the homogeneity region of the $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ solid solution becomes narrower near the composition $\text{NdBa}_2\text{Cu}_3\text{O}_z$ as the temperature decreases⁷⁵ and near the composition $\text{Nd}_2\text{BaCu}_3\text{O}_z$.^{63, 76, 78–81} In any case, the system becomes thermodynamically unstable as regards solid-phase decomposition in the region of subsolidus equilibria⁸² (see S.3).

This problem is of interest first of all owing to pronounced variation of the superconductivity parameters of the metastable $\text{R}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ solid solution depending on its state. Of great importance is also the degree of homogeneity of this solid solution, which depends on the preparation conditions and subsequent heat treatment. For instance, an increase in the parameter x of a solid solution homogeneous at the unit cell level can result in disordering of the oxygen sublattice in the basal plane due to the presence of additional amounts of REE^{7, 8, 76, 83–90} and in a reduction of the T_c value. If a solid solution decomposes with the formation of a heterogeneous mixture of particles of different compositions upon heat treatment, a mechanical mixture of phases with individual characteristics will be detected. A nanocomposite in which chemical inhomogeneity exists at a level comparable with the size of tens of unit cells can exhibit a fairly high T_c and nonlinear field dependence of superconducting properties (see Fig. 4).

It was reported that macroscopic phase segregation can occur in an atmosphere of elevated partial pressure of oxygen as a result of decomposition of supersaturated solid solution with the formation of barium cuprate.⁷⁶ The specific behaviour of single crystals on heat treatment⁸ is most probably due to a fundamentally different mechanism, which manifests itself, in particular, in the formation of a quasi-periodic tweed structure and in quasi-periodic spatial modulations of the ratio of concentrations of the elements constituting the single crystal (the so-called ‘compositional waves’). For instance, the Ba:Nd ratio in $\text{NdBa}_2\text{Cu}_3\text{O}_z$ varies from 2.0 to 0.7 (Fig. 8). Spinodal decomposition of the

$\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ solid solution, *i.e.*, its instability towards small fluctuations of x , resulting in phase demixing and eventually in the formation of coherent domains with appreciably different chemical composition, was suggested to be a possible reason for these changes.⁸ Reduction of temperature enhances the driving force of decomposition; however, its rate can be low because of extremely slow diffusion of components (the maximum rate of the process was experimentally observed at ~ 500 $^{\circ}\text{C}$, see also S.3). The possibility for spinodal decomposi-

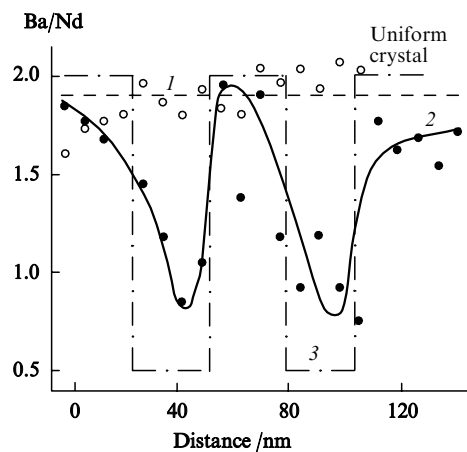


Figure 8. Quasi-periodic nanoscale fluctuations of the composition of $\text{NdBa}_2\text{Cu}_3\text{O}_z$ single crystals after low-temperature treatment at $p_{\text{O}_2} = 1$ atm. The composition of crystal matrix without nanoscale fluctuations (1, open circles) and with nanoscale fluctuations (2, filled circles); (3) variations of composition that should be observed upon the formation of interphase boundaries between the particles of decomposition products and the crystal matrix into which they are incorporated.

tion to occur was inferred from the experimental results obtained for the specimens prepared by zone melting⁹¹ and large-grain ceramics;^{70,92} it was also postulated (based on the data on the equilibrium phase diagrams⁸⁰) for a model of a regular-type solution with a high positive energy of interaction between the components ($\sim 40 \text{ kJ mol}^{-1}$).

Structurally, the segregation of a $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ solid solution can be represented as a local change in the occupation of the barium sites in the $\text{NdBa}_2\text{Cu}_3\text{O}_z$ structure, which results in the ordering of Nd^{3+} and Ba^{2+} ions in the BaO layer. The macroscopic picture of this phenomenon can be considered using the results of studies of the structure and properties of the $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ solid solution with a different degree of substitution (x).^{76,78,89,90} This substitution has two salient features. First, it is hetero-valent ($\text{Nd}^{3+} \rightarrow \text{Ba}^{2+}$, the 'hole' redistribution in the structure); second, this leads to the substitution of a smaller neodymium ion for larger barium ion (the ionic radii are 1.11 and 1.35 Å, respectively; internal 'chemical pressure').

The entropy of mixing of an ideal solution based on the $\text{NdBa}_2\text{Cu}_3\text{O}_z$ phase and a hypothetical compound $\text{NdNd}_2\text{Cu}_3\text{O}_z$ should be maximum for the composition $\text{NdBaNdCu}_3\text{O}_z$ (the Nd213-phase) (Fig. 9). Therefore, from the viewpoint of the entropy factor, the formation of a continuous series of $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ solid solutions with statistical distribution of Nd^{3+} and Ba^{2+} ions at the barium positions is the most favourable up to $x = 1$. However, the thermal stability of such a solid solution decreases as the degree of substitution x increases, *i.e.*, compression of the structure can result in a decrease in the formation energy of the crystal lattice due to the internal steric strain.^{76–81} The formation of the solutions with $x > 1$ is unfavourable both from the viewpoint of energy factors and because of the decrease in the contribution of the entropy of mixing.

Such an approach makes it possible to consider the solutions with $x = 1$ as a 'boundary' between real and hypothetical solid solutions. If the contributions of the entropy and energy factors are close, a distortion (puckering) of planar fragments of the structure can occur at $x \approx 1$, resulting in a new type of atomic ordering and in a reduction of the symmetry of the structure.^{78,89,90} Despite the fact that such a structural transition results in a decrease in the entropy of the system, a gain in the free energy owing to the increased energy of the lattice formation can be obtained in the case of partial relief of internal strain caused by the 'chemical pressure'. Therefore, different types of cation ordering can be observed within the homogeneity region of the $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ solid solutions, which is also accompanied by changes in the oxygen sublattice.

The results of investigations of the $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ solid solution ($0 \leq x \leq 0.9$) by X-ray diffraction (XRD) and Raman

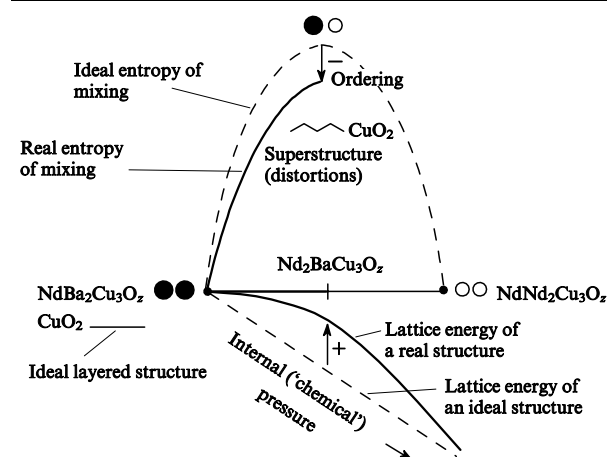


Figure 9. The effect of chemical pressure on the change in the structure of $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ solid solution.

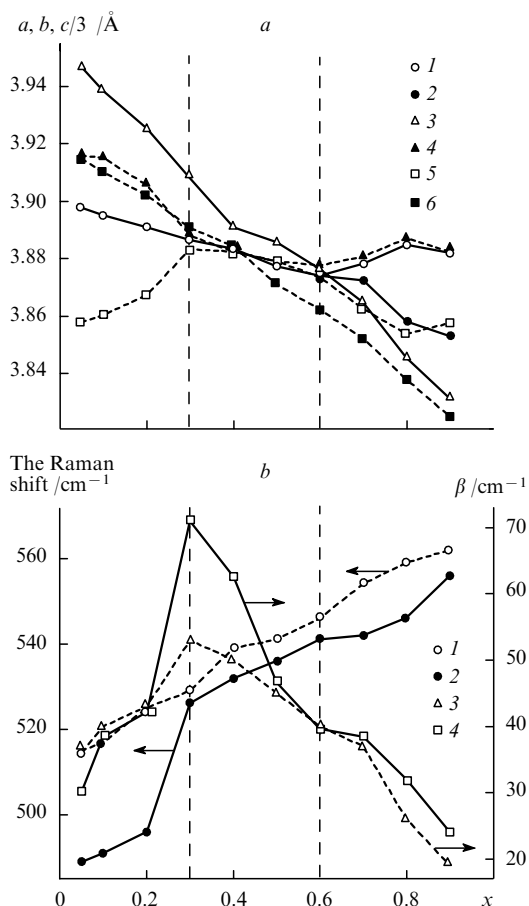


Figure 10. Results of investigations of $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ solid solutions by X-ray diffraction (a) and Raman spectroscopy (b); (a): unit cell parameters: (1 and 4) a ; (2 and 5) b ; (3 and 6) $c/3$; (1–3) quenching; (4–6) oxidation; (b): (1 and 2) the Raman shift; (3 and 4) broadening of an apical oxygen vibration mode (β); (1 and 3) oxidation; (2 and 4) quenching.

spectroscopy (RS) are shown in Fig. 10.^{89,90} The range of variation of x may conventionally be divided into three intervals, *viz.*, $0 \leq x \leq 0.3$, $0.3 \leq x \leq 0.6$ and $0.6 \leq x \leq 0.9$.⁷⁶ The specimens for which the degree of substitution x varies within the first interval have tetragonal or orthorhombic crystal lattices; the unit cell parameters a and $c/3$ ($a < c/3$) regularly decrease due to replacement of the Nd^{3+} ions of a smaller radius for the Ba^{2+} ions. The unit cell of the tetragonal phase ($a = c/3$) of the solid solution with x values within the second interval is characterised by an 'isotropic' compression of the unit cell, which occurs as x increases. An orthorhombic distortion of the unit cell is observed for compositions within the third interval. This distortion is retained even in the high-temperature region.^{81,89}

It was established in structural studies^{76,78,89,90} that the 123- and 213-phases[‡] are characterised by different types of ordering of the Nd^{3+} and Ba^{2+} cations, namely, 'vertical' ordering with the formation of uniform cation layers (Fig. 11) occurs in the former, whereas 'horizontal' superstructural ordering of barium ions and neodymium ions which replace the barium ions occurs in the latter. The appearance of a structure consisting of alternating chains of barium ions and those of neodymium ions that occupy the barium positions predetermines the ordering of oxygen ions. One of the oxygen positions along the shortest axis (b) in the high-temperature orthorhombic modification of the 213-phase is only partly occupied. Ordered rows of CuO_5 pyramids could be formed

[‡] In the phase diagram, they are terminating points of the existence region of solid solutions.

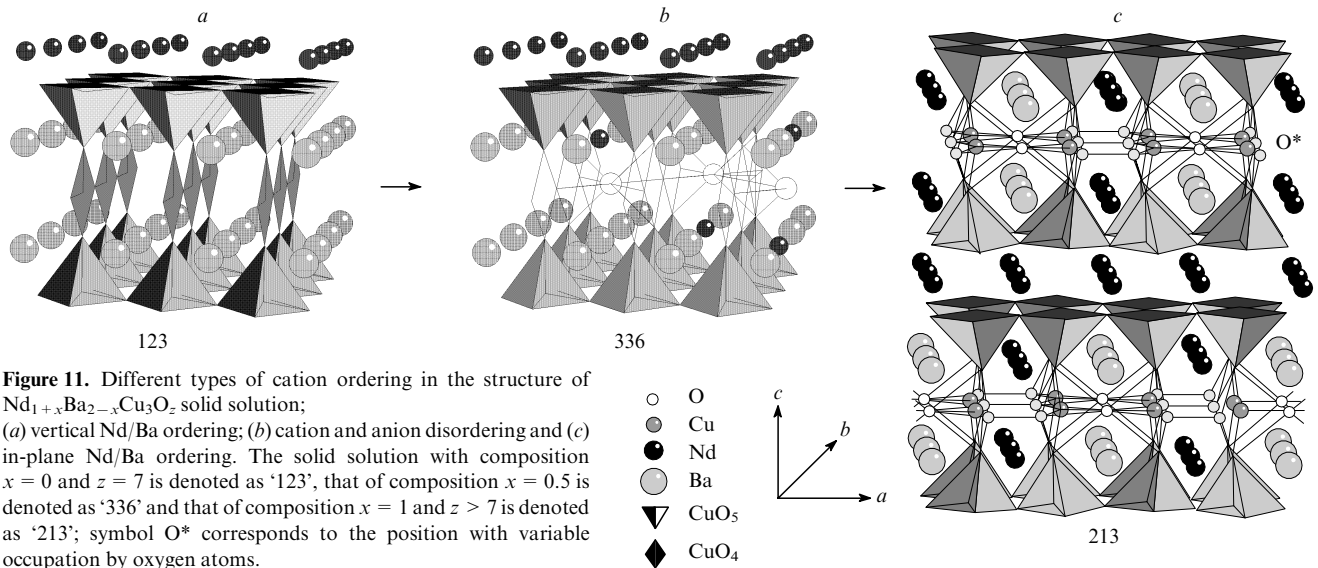


Figure 11. Different types of cation ordering in the structure of $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ solid solution; (a) vertical Nd/Ba ordering; (b) cation and anion disordering and (c) in-plane Nd/Ba ordering. The solid solution with composition $x = 0$ and $z = 7$ is denoted as '123', that of composition $x = 0.5$ is denoted as '336' and that of composition $x = 1$ and $z > 7$ is denoted as '213'; symbol O* corresponds to the position with variable occupation by oxygen atoms.

in the 'former' [BaO] block in the ideal (most oxidised) structure; however, a more complicated superstructural ordering in the real low-temperature orthorhombic modification of the 213-phase is observed. The temperature dependence of the oxygen content has an apparent sigmoid shape, which probably reflects this structural transition (at 700–720 °C in air⁸⁹) (see S.4).

The solid solution of intermediate compositions ($0.3 < x < 0.6$, the 336-phase) is tetragonal. Unlike the 123-phase, the 'vertical ordering' in this phase is distorted and a fraction of additional neodymium ions occupies the barium positions. At the same time, 'horizontal' ordering of cations in the barium positions does not occur yet in the 336-phase, which differentiates this phase from the 213-phase and results in disordering of the cationic sublattice.^{84–90} A maximum on the curve of the dependence of apical oxygen mode broadening in the Raman spectra on the composition of solid solution (see Fig. 10) corresponds to disordering of the oxygen sublattice.⁹⁰ It should be noted that analogous structural transformations result in changes in the hole distribution,^{84,87} which also pertains in greater degree of substitution in solid solutions. In this case the hole concentration in the superconducting CuO_2 planes decreases (the average, 'collective' charge of the plane decreases), whereas the average oxidation state of the copper atoms in the CuO_y plane of the dielectric (Nd,Ba)O block increases (see S.5).

Phase 'separation' of HTSC is a common phenomenon, which should be taken into account when analysing the phase relations in all the systems in question. For instance, it was postulated⁹³ that nonuniformity of oxygen distribution in the Y123-phase at a microscopic level is due to the spinodal decomposition. Low-temperature annealing of a single-phase solid solution $(\text{Bi,Pb})_2\text{Sr}_2\text{CaCu}_2\text{O}_z$ in the preparation of a bismuth-containing 2212-phase enriched with lead⁹⁴ resulted in its solid-phase decomposition with the formation of a lamellar nanostructure with alternating domains enriched with and depleted of lead. This decomposition should be extremely slow because of the low rate of cation diffusion, the necessity of overcoming the energy barriers associated with the formation of a solid-solid interface and elastic deformation of the matrix for phases with different molar volumes and crystal structure.^{8,75,82} In accordance with the Ostwald rule, the degree of supersaturation of a solid solution can be partially reduced in several intermediate steps, where a coherent or semi-coherent interface is formed in the matrix of the initial phase rather than requiring that the energy barrier to hetero-phase nucleation of a new phase is to be overcome. Differences in the lattice parameters of solid solutions of different compositions give rise to local structural strain.⁷⁵

Obviously, this problem requires studies of the initial stages of phase decomposition ('ageing' of the supersaturated solid solution) and construction of the so-called TTT (Time–Temperature–Transformation) diagrams for different initial states of solid solutions (ceramics, single crystals, films) as in the case of many alloys used in metallurgy.⁸² Mention may be made that solid-phase decomposition of HTSC can significantly improve certain practically important characteristics; in particular, this can be used for targeted formation of microscopic structural defects capable of acting as efficient pinning centres.^{7,8,94}

2. Phase relations in the supersolidus region

a. The use of the Gibbs phase rule

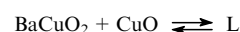
Experimental studies of phase relations in the supersolidus region and the development of realistic models of phase diagrams which fulfil the Gibbs phase rule are necessary for devising efficient methods for the preparation of high-temperature superconducting materials.^{8,9,53,61,64,74,75,95}

Experimental data on complex cuprate systems which would allow reliable calculation of the phase diagrams are extremely insufficient. Often, experimental phase diagrams (especially in the supersolidus region) are reported as being 'schematic' or 'tentative' ones, since they do not often fulfil the Gibbs phase rule. Nevertheless, several basic and doubtlessly reproducible characteristics (*e.g.*, melting temperatures and eutectic compositions) that are of great importance can be distinguished.^{61,95} The Y–Ba–Cu–O, Nd–Ba–Cu–O and Bi–Sr–Ca–Cu–O systems are a few examples of comprehensively studied high-temperature superconducting systems for which three-dimensional^{78,81,96,97} or multidimensional⁶⁴ models have been proposed for the description of phase relations.

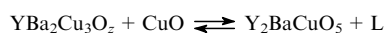
Numerous experimental studies^{96–108} and reviews^{13,21,22,63,100–102} have been devoted to the investigation and description of the phase diagram of parent Y–Ba–Cu–O system containing the high-temperature superconducting Y123-phase characterised by a very narrow cation homogeneity region. In particular, ~ 11 invariant reactions involving the melt (L) were found in the phase diagram of this system in the supersolidus region,⁹⁶ *e.g.*,



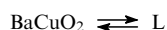
(a ternary eutectic at 890 °C with the liquid phase composition Y : Ba : Cu $\approx$ 1.0 : 32.5 : 66.5),



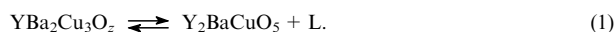
(a binary eutectic at 910–920 °C, ~ 69 mol. % – 71 mol. % of CuO),



(near 940 °C with the liquid phase composition Y : Ba : Cu $\approx$ 2.0 : 23.0 : 75.0),



(at ~ 1015 °C) and the peritectic decomposition reaction at 1000–1015 °C



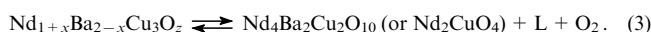
However, it should be noted that the peritectic decomposition temperature (T_p) of the Y123-phase appreciably decreases at low partial pressure of oxygen^{8,13,100,107} and increases at high pressure of oxygen (1–3000 atm), the phase relations in the system being changed in the latter case.¹⁰⁸ In both cases, the mechanism of decomposition of the 123-phase is also changed. Therefore, the simplified consideration of reaction (1) is incorrect. The peritectic decomposition reaction should be written as



where S and O₂ denote the melt, ‘secondary’ solid phases and the gaseous phase (oxygen), respectively.

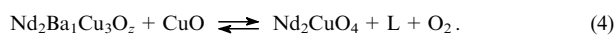
Therefore, the Y₂O₃–BaO–CuO–O₂ system should be considered as a quaternary system for which four phases (two solid phases, one liquid and one gaseous phase) are in equilibrium at the peritectic decomposition point of YBa₂Cu₃O_z. Obviously, such an approach makes it possible to fix the partial pressure of oxygen in the gas phase ($p_{\text{O}_2} = \text{const}$). An assumption can be made which is useful in studying many high-temperature superconducting systems that the gas phase consists of the only component (oxygen) and, therefore, the total pressure $p_{\text{tot}} = p_{\text{O}_2}$. This is incorrect in the case of thallium- and mercury-containing HTSC (see above). Hence, the transformation (2) can be conditionally considered monovariant at $p_{\text{tot}} = p_{\text{O}_2} = \text{const}$. In fact, a particular temperature of ‘melting’ (decomposition) of the 123-phase at fixed partial pressure of oxygen in the gas phase is observed, since it is necessary to introduce an additional condition (the cation stoichiometry), which imposes restrictions on the composition of the solid phase which undergoes decomposition.

This assumption is also valid if the decomposition of a solid solution follows the scheme^{76–81}



A substitution solid solution virtually degenerates into the stoichiometric 123-phase ($x \rightarrow 0$) at temperatures near peritectic melting. If both the cation composition (x) of the phase that undergoes decomposition and the partial pressure of oxygen are fixed, the experimentally determined peritectic decomposition temperature should have a unique value.

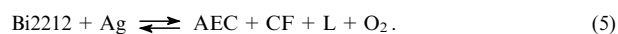
Interpretation of phase equilibria in R–Ba–Cu–O (R = Nd, Sm) systems would be incomplete without considering the recently reported data⁸¹ which suggest the existence of a five-phase equilibrium in the Nd-rich corner of the phase diagram.



Obviously, this equilibrium is invariant at fixed p_{O_2} (see S.6).

Investigation of bismuth-containing high-temperature superconducting systems also confirms the necessity of considering all restrictions imposed on the system and thus reduce the number of degrees of freedom. As in the case of Nd_{1+x}Ba_{2-x}Cu₃O_z system, the composition of phases that can be in equilibrium with the high-temperature superconducting phase at the point of peritectic decomposition, as well as the corresponding decomposition temperatures differ depending on the stoichiometric ratios of the cations constituting the high-temperature superconducting phase and on the p_{O_2} value in the gas phase. Consequently, the peritectic decomposition products of the Bi2212-phase (Bi_{2+δ}Sr_{2-x}.Ca_{1+x}Cu₂O_z) usually include different bismuthates [CF = Bi₂(Sr,Ca)_{3+n}O_{6+n}], alkaline-earth cuprates [AEC = (Sr,Ca)_nCu_mO_z] and a melt. Melting and crystallisation of

bismuth-containing composites are strongly affected by silver metal used as the sheath of ‘long-length’ tapes; the solubility of silver metal in the melt can reach up to 4 at. %–5 at. %.^{23,53,54,64} Therefore, the process of peritectic decomposition in this system can be represented as a six-phase equilibrium.



Practically, it is important that the partial pressure of oxygen changes not only the composition, but also the composition-dependent morphology of particles of the AEC and CF phases which coexist with the melt^{23,54} and, hence, the resulting microstructure of high-temperature superconducting tapes. It is obvious that a simplified analysis of the process (5), *e.g.*, without considering the effect of gaseous atmosphere (O₂) or silver, can lead to failures in developing new procedures for the preparation of bismuth-containing HTSC.

b. The surface of the liquidus

A realistic model of a phase diagram of a system in the super-solidus region is constructed on the basis of determination of melt composition and using the results of an analysis of the composition of the equilibrium solid phases. The solubility of REE oxides in cuprate melts was studied by differential thermal analysis (DTA), the dissolution-extraction method, quenching experiments, the ‘last droplet’ method, high-temperature microscopy and liquid-phase epitaxy (LPE) and single-crystal growth experiments.^{78–81,109–116} Unfortunately, in some instances the complexity of peritectic reactions, slow dynamics of establishing a true equilibrium with the gas atmosphere, supercooling of the melt, corrosion of crucibles used and contamination of the melt with impurities can make the results of DTA studies incorrect. The use of a direct melt sampling procedure during the quasi-equilibrium heating and cooling of melt in a temperature-controlled chamber made it possible to appreciably increase statistical representativeness and reliability of the results.^{109,111,113,114}

Generally, the solubility of REE oxides in a melt increases with an increase in temperature and partial pressure of oxygen, as well as in the case of REE with large ionic radii and at high copper oxide content.^{109,114} Tendencies of changes in the slope of the liquidus near T_p observed on going to REE with large ionic radii and on increasing p_{O_2} are similar. Practically, of most interest are the solubility of REE oxides and changes in the slopes of the liquidus near T_p , which make possible the prediction of the features of crystallisation in the systems under consideration. For instance, the content of yttrium in the melt at the peritectic decomposition temperature of the Y123-phase increases from 0.4 at. % at $p_{\text{O}_2} = 0.01$ atm (at 985 °C) to 0.6 at. % at $p_{\text{O}_2} = 0.21$ atm (at 1005 °C) and to 0.7 at. % in pure oxygen (at 1030 °C), whereas the neodymium content at $T_p = 1086$ °C (at 0.21 atm O₂) is several times higher (3 at. %). The content of neodymium in melts with high concentration of copper oxide can differ from that of yttrium by an order of magnitude (~ 7 at. % Nd at 1065 °C in air for the melt with a Cu : Ba ratio of 6 : 1).¹⁰⁹

Analysis of the solubility curves makes it possible to evaluate several important parameters, *viz.*, the dissolution enthalpy of the solid phase (it is determined from the slope of the liquidus),^{109,113–115} the peritectic decomposition temperature of the solid phase (it is determined from the bending of the solubility curve, since the dissolution enthalpies of 123- and 211-phases are different),^{113,114} the Gibbs standard energy of a peritectic reaction (when determining the solubility limits at different p_{O_2}).¹¹¹

The dependences of solubility of REE oxides on the ‘geometrical’ stability of R123-phases, which is determined by the ionic radius of REE, are shown in Fig. 12.^{8,63,81,113,114} As can be seen, the thermal stability of phases, characterised by the peritectic decomposition temperature, and the thermodynamic stability associated with the dissolution enthalpy of the solid phase in a melt increase as the ionic radius of REE increases. The same reason is also responsible for an increase in the ability of the melt to exist in the supersaturated state, since the smaller the slope of

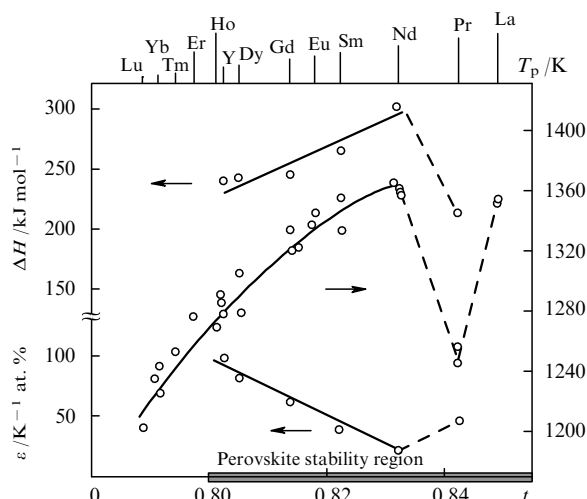


Figure 12. Dependences of thermal (T_p) and thermodynamic (ΔH) stability of $\text{RBa}_2\text{Cu}_3\text{O}_2$ -phases on the ‘geometrical’ stability of their crystal lattices (t) (at $p_{\text{O}_2} = 0.21$ atm); T_p is the peritectic temperature; ΔH is the dissolution enthalpy of R123 in the $\text{BaO} : \text{CuO} = 3 : 5$ melt; ε is the slope of the liquidus near T_p , which characterises the tendency to supersaturation; t is the Goldschmidt tolerance factor which reflects the ‘geometrical’ stability of the lattice.

the liquidus near the peritectic decomposition temperature, the higher the supersaturation at a given supercooling of the melt and the larger the amount of the substance that can be solidified. As has been mentioned above, these changes are explained by stabilisation of a defect perovskite-like lattice of 123-phases upon introduction of REE ions with large ionic radii (except for praseodymium, which drops out of the common dependence).

Establishment of the composition of the solid phase that is in equilibrium with a given melt is the key problem in the analysis of the liquid phase composition. Obviously — and this is of prime importance — knowledge of the liquid phase composition permits control of the structure and properties of the solid solution that directly depend on its composition. Actually, according to the Gibbs phase rule, the number of degrees of freedom for the ' $\text{R}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z + \text{L} + \text{O}_2$ ' equilibrium is $4 - 3 + 2 = 3$. Therefore, at a fixed temperature and partial pressure of oxygen, the solid phase composition is unambiguously determined by the melt composition. The dependences, which in combination with the equilibrium phase diagram can be used for predicting the composition of a solid solution with the maximum substitution degree, which can be crystallised from a melt of prescribed composition at a fixed temperature and partial pressure of oxygen, are shown in Fig. 13.⁷⁸⁻⁸¹

Distribution of the neodymium oxide between the solid solution and the melt is the most sensitive parameter of the equilibrium under consideration.^{80,81} The maximum on the curve of the content of neodymium oxide in the melt (see Fig. 13) is due to the influence of two oppositely directed factors, *viz.*, an increase in the neodymium content in the melt on an increase in the temperature and simultaneous decrease in the solubility limit of neodymium on the shift of the melt composition towards the BaO-rich region where a more thermally stable, less-substituted solid solution turns to equilibrium. In fact, the curve under consideration is a projection of the spatial trajectory of the point of ternary equilibrium 'Nd123ss-201-L' on the 'temperature-composition' plane. The equilibrium melt compositions of the solid solution depleted of and enriched with neodymium are strongly different and are shifted towards the region of Cu-rich compositions (Cu:Ba = 7:6 $\approx$ 5:3 for the 123-phase and Cu:Ba = 16:3 for the 213-phase). Quantitative analysis of the effects of the liquidus curvature near the '123-phase-melt' equilibrium showed that the substitution $x \approx 0$ is achieved in the

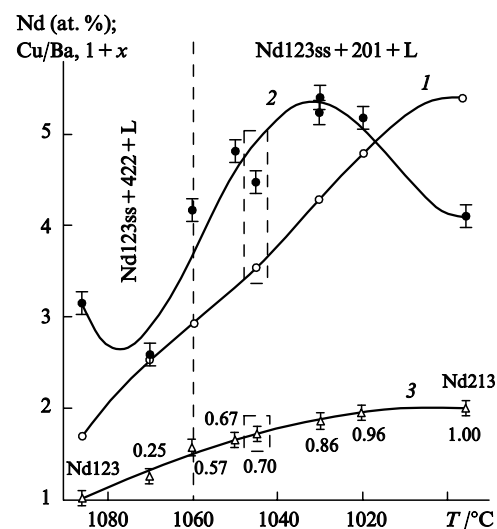


Figure 13. Temperature dependences of the Cu:Ba ratio (1), NdO_{1.5} content (2) in melt L and the (1 + x) parameter (3) of the solid phase of the Nd_{1+x}Ba_{2-x}Cu₃O_z solution coexisting in two-phase ‘Nd_{1+x}Ba_{2-x}Cu₃O_z + L’ equilibrium (at pO₂ = 0.21 atm). Numbers on curve (3) are the values of the parameter x.

case of crystallisation from melts enriched with barium oxide and on lowering the crystallisation temperature.⁷⁹

c. Characteristic features of polythermal sections

Technologically, the quasi-binary system ' $\text{Ba}_3\text{Cu}_5\text{O}_8$ '– $\text{Nd}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$ (Fig. 14*a*) is the most important since the compo-

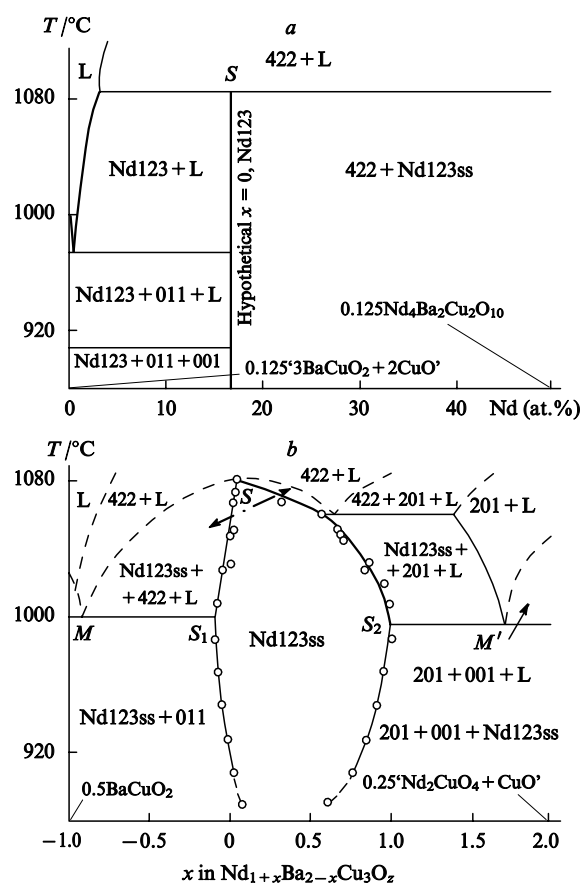


Figure 14. Most practically important quasi-binary polythermal sections of the Nd–Ba–Cu–O system (at $p_{O_2} = 0.21$ atm).

sitional point of the 123-phase belongs to this section. This can significantly simplify the consideration of transformations in this system. Investigations into phase relations in the vicinity of the 123-phase showed that the region of two-phase 'Nd123-phase-liquid' equilibrium in air lies in the temperature range 970–1090 °C (at $p_{O_2} = 0.21$ atm).^{110–113}

The region of solid solutions based on the 123-phase belongs to another important $BaCuO_2$ –'Nd₂CuO₄–CuO' quasi-binary section (Fig. 14b).^{63, 76, 78} Invariant transformations involving the liquid phase ($MS_1 \sim 1000$ °C, $M'S_2$, 990 °C) characterise the highest probability of synthesising the solutions with the minimum (S_1) and maximum (S_2) substitution degrees. However, if the reaction with the 213-phase is fairly well studied,^{78, 81} it is difficult to carry out quantitative studies of equilibria with the 123-phase because of the very large slope of the solidus in the vicinity of the (S_1) point.^{75, 79} It should be noted that the appearance of a liquid in this section with the increase in the temperature near the 123-phase is explained by the melt field propagation towards the $BaCuO_2$ phase. According to the reported data,^{78–81} the increase in temperature shifts the composition of the melt which is in equilibrium with 123- and 422-phases away from the point corresponding to barium cuprate because of the extension of the two-phase '422 + L' field. The maximum peritectic decomposition temperature of the 123-phase (S , ~ 1085 °C) is achieved for those compositions that somewhat deviate from the ideal 123-phase (partial substitution of Nd for Ba). This fact is mistakenly ignored in some communications.

The composition of a solid solution with the maximum peritectic decomposition temperature T_p returns almost completely to the 123-composition only after appreciable reduction of the partial pressure of oxygen.⁷⁵ For instance, the composition of the solid solution with the maximum T_p is characterised by $x \approx 0.1$ in oxygen, $x = 0.05$ in air and $x \approx 0.0$ at $p_{O_2} = 10^{-3}$ atm. No solid solution based on the 123-phase is present in the system above the maximum temperature of peritectic decomposition (the '422 + L' field). Below this temperature, the solid solution region is 'gripped' from both sides by the '422 + Nd123ss + L' three-phase field. At 1060 °C, the '422–Nd123ss–L' tie-triangle becomes geometrically impossible for compositions with $x > 0.6$ ⁸¹ and a decrease in temperature leads to establishment of equilibrium between the most neodymium-rich solid solution, neodymium cuprate and the melt. The slope of the solidus changes correspondingly.⁸⁰ As has been mentioned above, below 990 °C the solid solution is in equilibrium with other two solid phases (CuO and Nd_2CuO_4).

Thus, this type of systems is characterised by the following qualitative features.

1. The region of the solid solutions based on high-temperature superconducting phases can be rather extended. The problems of determining the composition of solutions with the lowest substitution degree and of the existence of solutions with Ba^{2+} substitution for R^{3+} in R – Ba – Cu – O systems (see Refs 7, 63, 76, 117) are poorly studied.

2. The decomposition temperature of a solid solution can vary over a wide range depending on its composition. This is probably associated with the complicated character of the cation ordering within the homogeneity region. The shape of the solidus near the maximum T_p (a sharp or flattened maximum) can provide information on the type of the solid solution, daltonide or berthollide that is formed.

3. As a rule, the reduction of p_{O_2} results in a change in the shape of the homogeneity region of the solid solution. In particular, the decomposition temperature of the solid solution and the slope of the solidus are changed and a narrowing or (more rarely) broadening of the homogeneity region is observed.

4. The compositions of equilibrium phases in the supersolidus region are different, which depends on the composition of the solid solution based on the high-temperature superconductor. Particular emphasis should be placed on quantitative determination of the equilibrium tie-lines in the 'solid solution–melt' two-

phase region. Each tie-line is unique; therefore, the choice of a particular compositional point on the phase diagram (all other conditions being constant) determines not only the possible type and weight ratio of the coexisting phases, as in the case of the Y – Ba – Cu – O system, but also the chemical compositions of these phases and, hence, the physical properties of the crystallising solid solution. Determination of the actual chemical compositions of the coexisting phases is also necessary to avoid the errors when constructing the phase diagrams.

5. As a rule, polythermal quasi-binary sections of high-temperature superconducting systems are characterised by certain temperatures of invariant transformation (in this case, at about 1000 °C, see Fig. 14). Below this temperature, liquid phases disappear and the equilibrium between solid phases is established.

6. The narrowing of the homogeneity region can occur below the above-mentioned temperatures. In other words, solid solutions with the highest (lowest) substitution degrees appear to be less stable at both higher and lower temperatures. Analysis of this temperature region is closely related to studies on the decomposition dynamics of supersaturated solid solutions, the formation of a particular nanostructure and to changes in physical characteristics of the system.

3. Melt crystallisation mechanisms

a. Single-crystal growth

Peritectic decomposition is a salient feature of all oxide superconductors, which is due to their multicomponent composition and structural complexity. Crystallisation involves two different phases (the crystal and the mother liquid/melt) separated by a mesophase layer, which is a thin layer of the melt immediately adjacent to the solid phase.⁸ The components are transferred from one phase (the 'mother' or nutrient phase) to the other phase (crystal) as this interface moves. In turn, the rate of the process can be limited by the kinetics of deposition of the substance on the crystal face, diffusion of the substance from the surrounding phase as well as by dissipation of the latent heat of crystallisation.

Crystallisation cannot proceed in the absence of the driving force (supersaturation, supercooling or metastability of homogeneous 'mother' phase). In the case of crystallisation from the solution or melt, the driving force is often represented as the relative supersaturation of the melt

$$\sigma = \frac{c_1 - c}{c_1},$$

where c_1 is the equilibrium (under given conditions) concentration in the melt of the component transferred to the solid phase and c is its running value. The region of supersaturated solution is divided into the region of metastability and the labile region. The interface between these regions corresponds to maximum supersaturation in the system that can be achieved until spontaneous crystallisation begins.⁸ For the Y123-phase, this region is rather narrow (0.8 °C in air with respect to supercooling).¹¹⁸

Investigations of the primary crystallisation field (PCF) are important when considering single-crystal growth. Unfortunately, the PCF boundaries have not been reliably determined yet even for the Y123-phase, though it is obvious that the PCF does not include the melt of the 1:2:3 stoichiometric composition. In different studies, the ratios of barium and copper oxides ($Ba:Cu$) for PCF were estimated at 17:83–44:56, 24:76–46:54, 18:82–46:54 and 24:76–42:58, whereas the yttrium content (at. % Y) varied in the range 3.0–5.0, 1.0–2.0, 2.0–4.0 and 0.5–3.5, respectively.¹³ Crystallisation of the $Nd_{1+x}Ba_{2-x}Cu_3O_z$ solid solution with $x > 0.7$ from the $Ba:Cu = 3:12$ melt has been reported.¹⁰⁹ The composition of the solid solution changed during isothermal annealing. Artifacts in the determination of the PCF (especially using thermal analysis) often arise because of the absence of local equilibrium with the gas phase; therefore, data on PCF should be interpreted carefully. In some instances, the results of determination of the position of the

liquidus surface should be used instead. The most important problem is the search for chemical additives that extend the PCF and allow the single-crystal growth over wider temperature and concentration ranges. Most often, BaF_2 , Bi_2O_3 , B_2O_3 , Ag and BaCl_2 are used as such additives.^{13, 119–121}

If a crystal face contacts the metastable ‘mother’ phase, it can grow. Several main growth mechanisms exist under conditions of fast diffusion of the components of the crystallising substance and the absence of problems with dissipation of the heat of crystallisation.⁸ Depending on the driving force of crystallisation, continuous growth (face deposition), ‘island’ growth due to two-dimensional nucleation and spiral growth along the screw dislocations can be observed.

The last-named mechanism is the most probable for ordinary solution/melt supersaturations; the first two mechanisms are observed very rarely because of the high activation energy of the processes.⁸ The ‘Terrace-Ledge-Kink’ (TLK) growth of the crystal due to the ‘sliding’ of the crystallising layers of the moving terraces over the surface is also characteristic of high-temperature superconducting materials,⁸ whereas renucleation on the defects of the ‘two-dimensional angle’ type (the so-called ‘Twin-Plane-Re-entrant-Edge’ or TPRE growth) occurs much more rarely and was detected in high-temperature superconducting systems only recently (Fig. 15).⁸¹ In real systems, the common events are (i) crystal face formation as a result of complex interaction of several crystallisation centres, (ii) combination of several growth mechanisms, (iii) growth due to the formation of macroscopic spirals and

terraces, *etc.* Currently, the morphology of growth of the spirals of R123-phases and its dependence on the crystallographic indices of the crystal face,^{122, 123} the degree of supersaturation, temperature and the nature of REE are well studied.^{124–126}

b. Evolution of a polycrystalline system

The behaviour of the peritectic melt[§] obeys general regularities of crystallisation of an individual crystallite from the homogeneous melt. At the same time, analysis of this system is rather complicated and should be performed with consideration of the interactions between the melt and both the properitectic and gas phases that coexist at the peritectic decomposition point of HTSC. Additionally, the fact that crystallisation of a peritectic melt results usually in the formation of a polycrystalline product should be taken into account.

When polycrystalline HTSC are prepared using melt crystallisation techniques, their microstructure is formed under non-equilibrium dynamic conditions. Hence the problem arises of the search for methods of reproducible preparation of materials comprising well-shaped crystallites with an optimum size and optimum mutual orientation and sufficiently strong intercrystallite contacts. From this point of view, the most interesting is to analyse the regularities of the formation and evolution of an ensemble of crystallites at both small and large deviations of the system from the equilibrium state. Three types of crystallisation models of REE-containing cuprates are known, in which the interaction in the 211-phase–melt subsystem is considered. These are phenomenological models of the interaction between the particles of secondary phases and the melt, computer models of this interaction and mathematical models of propagation of the crystallisation front of the high-temperature superconducting phase and changes in its morphology. The models of REE-containing melt crystallisation with inclusion of interactions in the ‘gas phase–melt’ subsystem are much less developed.

Superconducting phases are mainly formed owing to dissolution in the melt of ‘secondary’ phase particles, followed by homogeneous formation of the high-temperature superconducting phase in the melt.^{8–11, 127–130} In the vicinity of the surface of the particles of the 211-phase, the melt is enriched with yttrium and the crystallites of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ phase are formed near the surface of these particles rather than at the ‘211-phase–melt’ interface. Crystallisation is accompanied not only by ‘pushing’ large particles of the 211-phase by the growing faces of crystallites of the 123-phase, but also by their trapping by the bulk of the growing crystallites. The formation of crystallites of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ -phase is preceded by an induction period, after which crystallisation proceeds in the bulk at an abnormally high rate. Different melt crystallisation models are presented in Table 3.

Mention should be made of considerable interest in the computer simulation of crystallisation processes. Different computer models and simulation concepts are used (*e.g.*, ‘cellular automata’ and diffusion-in-melt models and the phase field concept for multiphase systems, see S.7). It can be assumed that solidification of a peritectic melt can proceed in different ways depending on the parameters of the initial state of the melt, which results in the appearance of three different crystallisation regions characterised by particular final microstructure of polycrystalline materials.^{127, 128} The provision of stable crystallisation of the superconducting phase owing to stabilisation of the nucleation process is the most important condition for the preparation of high-temperature superconducting materials with high output characteristics.

The experimental proof of this statement was obtained in studies of the doping of melts with REE oxides.^{128, 129} The melt

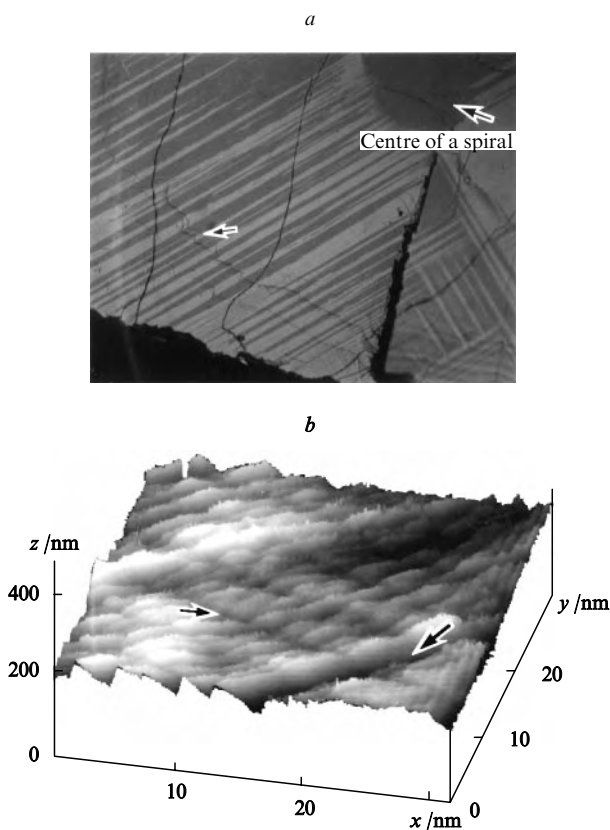
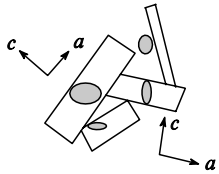
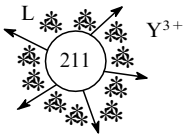
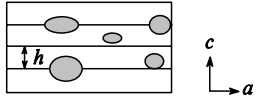
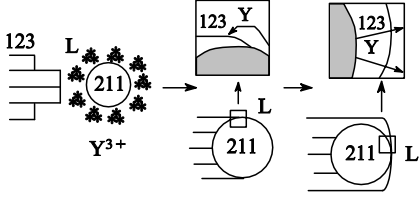
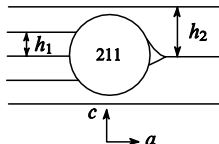
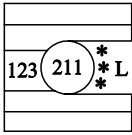
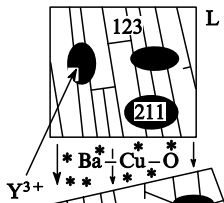
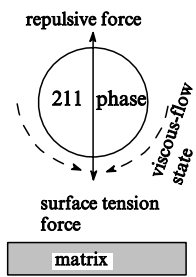
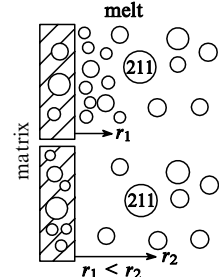
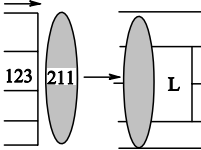
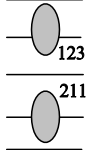


Figure 15. The mechanism of crystal growth in high-temperature superconducting systems (the $\text{Nd}_{1.85}\text{Ba}_{1.15}\text{Cu}_3\text{O}_x$ -phase) by renucleation on defects of the ‘dihedral angle’ type (the so-called ‘Twin-Plane-Re-entrant-Edge’ or TPRE growth);⁸¹

(a) general view of the growing crystal face: twins are crossed by microscopic cracks arisen after thermal shock on detaching the crystal from the melt surface; the crystallisation front of the ‘tail’ of growth spirals that form a visually observed macroscopic spiral moving along the twinning direction at a higher velocity; (b) the structure of twins according to atomic force microscopy data; the twin boundaries are indicated by arrows.

§ Hereafter a ‘peritectic melt’ is meant a system consisting of a liquid and a solid (high-temperature, properitectic) formed upon peritectic decomposition of the HTSC.

Table 3. Crystallisation mechanisms of peritectic melts.

Model	Morphology of particles of a 211-phase	Proposed scheme of the interaction	Result of interaction	Ref.
Heterogeneous nucleation	any			6
Dissolution in melt and homogeneous nucleation	isotropic (spheres)			6, 8
Edge effects, entrapment of particles of the 211-phase by the crystallisation front	highly disperse particles			9, 11
Formation of 'gaps' and displacement of the melt to grain boundaries on trapping the particles of the 211-phase	large particles			9, 11
'Pushing-and-trapping' of particles of the 211-phase by the crystallisation front ^a	—			8
Dispersion of particles of the 211-phase by the moving crystallisation front	anisotropic particles (needles)			9, 11

^a The mechanism is determined by particle size, the energy of surface interaction and by the crystallisation rate.

analysed contained $\sim 80\%$ of Cu(I), which was confirmed by the results of quenching experiments and chemical analysis,^{55, 129} by BaCu_2O_2 observation using X-ray phase analysis^{13, 129, 131} and by *in situ* measurements of the EXAFS spectra of the melt.^{132, 133} Cooling of the melt results in the recovery of the initial oxygen content, which occurs more easily with an increase in the partial pressure of oxygen in the gas phase.

In principle, the transformation $\text{Cu(I)} \rightarrow \text{Cu(II)}$ provides a possibility for crystallisation of a non-superconducting phase of barium cuprate BaCuO_2 to occur. This is favoured by the presence in the melt of the components necessary for the crystallisation of BaCuO_2 and by the fact that the temperature of its crystallisation in air⁹⁶ and the crystallisation temperature of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ -phase are close. In other words, a 'bifurcation'-like situation occurs in the 211-phase–melt system, which can be followed by crystallisation of either yttrium–barium cuprate $\text{YBa}_2\text{Cu}_3\text{O}_x$ or barium cuprate BaCuO_2 .^{127–129} It is this phenomenon that is

observed experimentally. In these cases, the direction of crystallisation depends on many factors (which are often ignored) such as the oxidation rate of the melt during its cooling, the rate of dissolution of the Y_2BaCuO_5 -phase in the melt, the partial pressure of oxygen in the system, the gradients of both the temperature and oxygen pressure at the gas phase–melt interface and, finally, the prehistory of the sample and its size. Because of this, small deviations from the empirically established conditions for the synthesis of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ phase immediately result in undesirable formation of non-superconducting cuprate phases even in high-density specimens and in dramatic deterioration of properties of the high-temperature superconducting material prepared.

Crystallisation of the 123-phase can probably be the major process in the system if nucleation begins at a temperature which is higher than the crystallisation temperature of BaCuO_2 . Superconducting layered yttrium–barium cuprate is the only phase

whose specific crystal structure can be selectively affected by the doping of the melt with REE ions. This makes it possible to experimentally distinguish between the melting temperatures of binary non-superconducting and ternary superconducting cuprates, thus performing targeted crystallisation of the high-temperature superconducting phase from a multicomponent melt.^{128, 129, 134, 135}

The general pattern of the process can be changed dramatically upon a decrease in the partial pressure of oxygen in the gas phase. Oxidation becomes the limiting stage of crystallisation in an oxygen-deficient atmosphere.^{129, 135} Copper (Cu^{2+}) ions formed upon melt oxidation are bound by the excess R^{3+} and Ba^{2+} ions to form the $(\text{R}, \text{Y})\text{Ba}_2\text{Cu}_3\text{O}_z$ -phase; however, no rapid crystallisation of the nonequilibrium product (binary barium cuprate) is observed. Thus it can be assumed⁵⁵ that the formation of the phase and microstructure of the material are strongly affected by three main factors. These are (i) the total flux of yttrium (REE) ions j_Y from the surface of the 'green-phase' particles to the melt, which is mainly determined by dispersity of the particles and by the surface energy of the interface; (ii) the oxygen flux j_O to the crystallising melt, which depends on both the partial pressure of oxygen in the gas phase and geometric characteristics of the specimen and (iii) the heat flux j_Q evolved from the specimen during its cooling, which is determined by the heat treatment regime.

Thus, the optimum procedure for preparation of high-quality high-temperature superconducting materials should take into account simultaneous and mutually dependent changes in these most important parameters of the process.

4. Oxygen nonstoichiometry of high-temperature superconducting phases

The oxidation stage is of particular importance when preparing, e.g., the $\text{RBa}_2\text{Cu}_3\text{O}_z$ superconductors with a wide oxygen homogeneity region ($z = 0-1$).^{1, 2, 8, 13, 17, 22, 50, 100, 108} For bismuth-, thallium- and mercury-containing high-temperature superconducting phases, the homogeneity region is much narrower.^{17, 56, 67, 69, 101} On the contrary, several high-temperature superconducting materials [e.g., the 'electron'-type (Nd , Ce) CuO_{4+y} HTSC] require annealing in a reductive atmosphere.² In all cases, there are strong reasons for detailed investigation of the oxygen nonstoichiometry of HTSC. Here, it is well to bear in mind the following.

1. The oxygen content is correlated with the concentration of charge carriers, whose optimum value provides the maximum T_c value (a T_c 'dome'). 'Underdoped' ('underoxidised') or 'overdoped' ('overoxidised') phases can have a much lower T_c (Fig. 16). In the general case, it is the concentration of the charge carriers localised on particular elements of the structure that determines the physical phase diagram of HTSC (see Fig. 3).¹⁶

2. Changes in the oxygen content can result in significant changes in the phase stability and in structural phase transitions. For instance, ferroelastic $\text{RBa}_2\text{Cu}_3\text{O}_z$ -phases undergo an 'order-disorder' second order phase transition which is accompanied by a tetragonal-to-orthorhombic distortion of the crystal lattice and simultaneous formation of extended twins.^{8, 22, 93, 126} The changes in thermodynamic characteristics of high-temperature superconducting phases with different oxygen content can result in the appearance of the low-temperature stability threshold,^{50, 51, 75, 106} phase separation in such solid solutions and in nonuniform oxygen distribution over the superconducting matrix.^{8, 93}

3. Investigations of oxygen diffusion in high-temperature superconducting phases is not only of practical, but also of theoretical importance since the diffusion coefficient is a 'structurally sensitive' quantity, which depends on the concentration of oxygen vacancies (and, hence, on specific features of the equilibrium p_{O_2} - T - z -diagram), their ordering (the crystal lattice symmetry of the high-temperature superconducting phase and second order phase transitions, effects of various types of

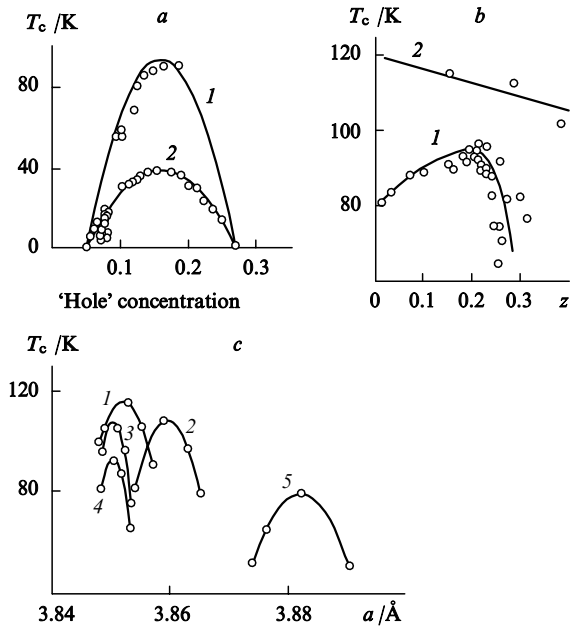


Figure 16. Dependence of the transition temperature to the superconducting state on the 'hole' concentration (a), oxygen nonstoichiometry (b) and unit cell parameters which are determined by the oxygen content (c) for the most abundant types of HTSC; (a): $\text{YBa}_2\text{Cu}_3\text{O}_z$ -phases (1) and $(\text{La}, \text{Sr})_2\text{CuO}_{4+y}$ (2); (b): $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+z}$ (1) and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+z}$ (2); (c): the $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+z}$ homologous phases, Hg1223 (1), Hg1212 (2), Hg1234 (3), Hg1245 (4) and Hg1201 (5).

substitution in the structure), the energy parameters of different oxygen sites (the activation energy and the probability of exchange between the oxygen positions, etc.). A rather high anisotropy of the diffusion coefficients along the main crystallographic directions can indicate a layered structure of the HTSC (two-dimensional diffusion in CuO_y planes in which the vacancies are concentrated, etc.). Relatively large absolute values of the diffusion coefficients of high-temperature superconducting phases compared to those of other systems¹³⁶⁻¹³⁹ indicate that they are highly defective. Studies of the diffusion mechanism give useful information on the different types of the oxygen bonding in the structure.¹⁴⁰ Finally, parameters of the oxygen diffusion can essentially depend on the size of grains of the high-temperature superconducting phase, the quality of their surfaces, specific features of the interface between the superconducting and gas phases, the presence of internal microscopic strain, etc. Thus, analysis of these dependences makes it possible to obtain information on the real structure of high-temperature superconducting materials. The results of the diffusion studies can be used for determination of thermodynamic properties of high-temperature superconducting phases.

a. Phase diagrams of $\text{RBa}_2\text{Cu}_3\text{O}_z$ - O_2 systems and the oxygen ordering processes

The problem of oxygen nonstoichiometry in $\text{RBa}_2\text{Cu}_3\text{O}_z$ - O_2 systems and related phenomena are extremely complicated.^{13, 100, 141-148} Different types of diagrams used to represent the oxygen nonstoichiometry in high-temperature superconducting phases of the Y-Ba-Cu-O system are shown in Fig. 17.

The p_{O_2} - T - x - z -diagram presented in Fig. 18 illustrates the effect of cation ordering on the 'behaviour' of the oxygen sublattice in the $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ solid solution.⁸⁹

Obviously, the temperature, total pressure and partial pressure of oxygen in the system affect significantly the oxygen content in the HTSC-phase, peculiarities of oxygen ordering and symmetry of the crystal lattice of this phase, the stability of various homologues of the high-temperature superconductors (123-, 247-

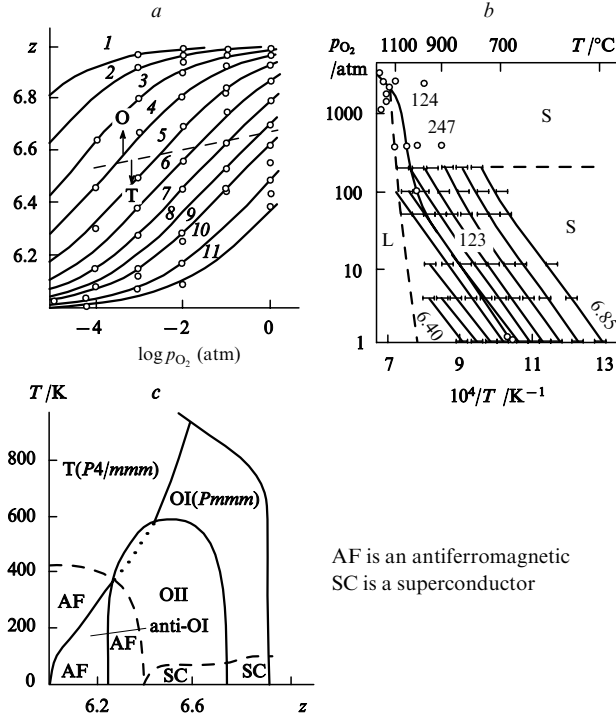


Figure 17. Types of representation of the diagrams of equilibrium oxygen content in $\text{YBa}_2\text{Cu}_3\text{O}_z-\text{O}_2$ systems; (a): $p_{\text{O}_2}-T-z$ -diagram; T/K : (1) 573; (2) 623; (3) 673; (4) 723; (5) 773; (6) 823; (7) 873; (8) 923; (9) 973; (10) 1073; and (11) 1173; (b) phase relations at a high pressure of oxygen, the z value varies from 6.40 to 6.85; (c) calculated low-temperature diagram of oxygen content in the Y123-phase and different types of ordering of the oxygen sublattice.

or 124-phases) and that of the high-temperature superconducting phase against peritectic and/or solid-phase decomposition.

The highest T_c values are achieved at the optimum oxygen content in the high-temperature superconducting phase.¹⁴⁸ The $(T_c)_{\text{max}}$ values for $\text{YBa}_2\text{Cu}_3\text{O}_z$ are 93.5 K at $z = 6.94$ and 87 K at

$z = 7.0$ and 6.85. ‘Heavy’ REE of the yttrium subgroup with smaller ionic radii form 123-phases for which $(T_c)_{\text{max}} < 90$ K, which means that the maximum value is shifted towards lower oxygen content. For instance, $(T_c)_{\text{max}} = 87$ K at $z = 6.90$ for $\text{YbBa}_2\text{Cu}_3\text{O}_z$. On the contrary, HTSC containing ‘light’ REE are characterised by higher $(T_c)_{\text{max}}$ values at higher oxygen content. Probably, the $(T_c)_{\text{max}}$ values of $\text{NdBa}_2\text{Cu}_3\text{O}_z$ with $z = 7$ and its analogue $\text{LaBa}_2\text{Cu}_3\text{O}_z$ with $z > 7.0$ reach 96 K^{7,8,43,86} and 98–100 K,⁸⁶ respectively. High oxidation degrees of these phases are achieved by heat treatment at low temperatures (350 °C) and high pressure of oxygen (100–900 atm).^{7,8,92} The effect of ionic radii of REE on T_c of the 123-phases is explained^{17,42,43} using the model of charge redistribution between the superconducting CuO_2 planes and dielectric CuO_y blocks in the structure under conditions of internal chemical pressure (followed by compression or expansion of the structure) which results from changes in the geometrical size of cations occupying the sites of REE ions. Analogous dependences are also known for other cuprate superconductors and the optimum oxygen content is different for different HTSC homologues (see Fig. 16c).

The formation of twins owing to relaxation of internal strain which appears upon orthorhombic distortion of a tetragonal unit cell in the course of oxygen diffusion into the grains of superconductor is clear evidence of the ordering of oxygen atoms in the unsubstituted 123-phases. The distance $\Delta\lambda$ between the twin boundaries in the twin ensemble varies in accordance with the formula:¹⁴⁹

$$\Delta\lambda = \left(\frac{128\pi\gamma G}{ES} \right)^{0.5},$$

where γ is the specific energy of the twin boundary, G is the size of twinned grain, E is the elastic modulus of the material and S is the coefficient of orthorhombicity.

Thus, one can expect that the largest twins will be formed in single crystals and that the size of these defects will to a great extent depend on the elasticity and ‘degree of orthorhombicity’ of the material used. Twinning results in microscopic cracking of melt-solidified ceramics. Perfect specimens can be obtained using both the single-crystal detwinning and twin-free crystal growth methods.^{150,151}

b. Diffusion of cations and anions

Oxygen diffusion in high-temperature superconducting phases has been studied using different methods such as dynamic¹⁵² and isothermal¹⁵³ thermogravimetry, electrochemical potentiometry,¹⁴³ $\text{O}^{18}/\text{O}^{17}$ tracer diffusion method,^{154–156} determination of internal friction coefficients,¹⁵⁵ *in situ* measurements of electrical resistivity,¹⁵⁷ direct observations of the twinning front propagation in single crystals,^{158,159} method of isotope exchange with the gas phase^{160,161} and computer simulation using the cellular automata method.¹⁴⁷ The diversity of methods used and factors affecting the oxygen diffusion explains a great scatter (several orders of magnitude) of results obtained by different groups of researchers. Nevertheless, mention may be made of several important regularities.

1. One must discriminate between the coefficients of self-diffusion D_{self} and the coefficients of chemical diffusion of oxygen D_{chem} in high-temperature superconducting phases related by a simple formula¹⁵⁷

$$D_{\text{chem}} = D_{\text{self}}\Phi,$$

where Φ is the so-called thermodynamic factor. Usually, the Φ value is nearly constant if the oxygen content z in the R123-phases lies in the range from 6 to 6.8; however, it increases rapidly as z approaches the value corresponding to the most oxidised state ($z = 7$). As a rule, the D_{chem} value is 4–5 orders of magnitude higher than that of D_{self} .

2. For polycrystalline materials based on the Y123-phase, the D_{chem} and D_{self} values vary in the ranges 10^{-5} – 10^{-11} and 10^{-9} – 10^{-13} $\text{cm}^2 \text{ s}^{-1}$, respectively. The activation energies of

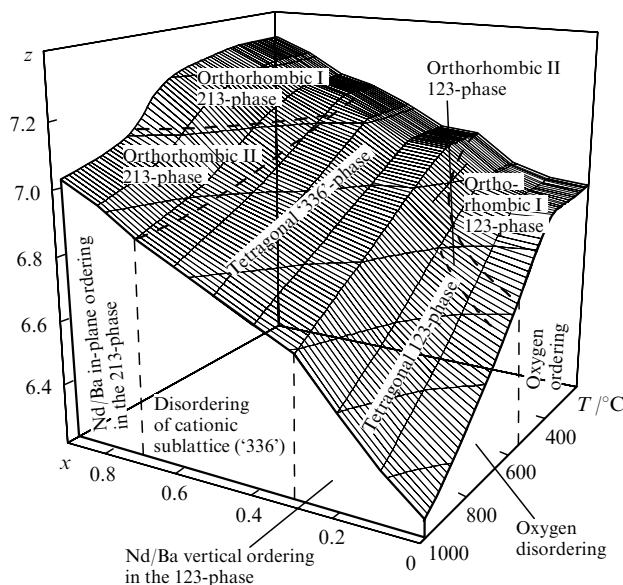


Figure 18. Section of the $p_{\text{O}_2}-T-x-z$ -diagram of the $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z-\text{O}_2$ system at $p_{\text{O}_2} = 0.21$ atm, which illustrates the effect of the character of cation ordering on the equilibrium oxygen content in this solid solution.

self-diffusion in the R123-phases decrease as the ionic radii of REE increase.¹⁴³

3. For single crystals, the coefficient of self-diffusion of oxygen along the c axis at 400 °C ($D_c = 10^{-16} - 10^{-17} \text{ cm}^2 \text{ s}^{-1}$) is six orders of magnitude lower than for polycrystalline samples (D_{poly}), whereas the rate of diffusion along the b axis at 300 °C in detwinned crystals ($D_b = 2 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$) is at least two orders of magnitude higher than that of diffusion along the a axis ($D_a = 5 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$).¹⁵⁴ Thus, self-diffusion in single crystals is highly anisotropic and proceeds almost completely in the ab plane [$D_{ab} = D_{\text{poly}} = (10^4 - 10^6)D_c$, $D_b = 100D_a$, $D_b = 10D_{ab}$]. At the same time, the coefficient of chemical diffusion for these types of single crystals lies in the range $10^{-8} - 10^{-7} \text{ cm}^2 \text{ s}^{-1}$.

4. Second order phase transitions, occurring on ordering or disordering of the oxygen sublattice, must result in jumpwise changes in the diffusion coefficients. This is confirmed by the results obtained in the studies of diffusion coefficients of $\text{RBa}_2\text{Cu}_3\text{O}_z$ ($R = \text{Y}$ and Nd) phases over a wide range of temperature and partial pressure of oxygen.¹⁴³ According to the reported data, the rate of oxygen diffusion in the orthorhombic phase is higher than that in the tetragonal phase despite the fact that the number of available oxygen vacancies in the latter is larger than in the former. Probably, this indicates changes in the elementary mechanism of the process.

The role of mobility of the cationic sublattice is at least as important as, and in some instances even more important than, that of oxygen diffusion; however, it has been much less studied.¹³⁶⁻¹⁴⁰ Migration of cations in single crystals of oxide superconductors follows ordinary diffusion mechanisms (vacancy-type, interstitial, dissociative, along dislocations and point defects); in polycrystalline HTSC, diffusion along the grain and pore surface, twin boundaries, *etc.*, is additionally observed.¹⁴⁰

Self-diffusion of Cu^{2+} in the $\text{YBa}_2\text{Cu}_3\text{O}_z$ phase was studied by the tracer diffusion method.¹³⁷⁻¹³⁹ The activation energy of this highly anisotropic process lies in the range 165–255 kJ mol^{-1} and the diffusion coefficient at 780–900 °C lies within the limits $\sim 5 \times 10^{-12} - 10^{-13} \text{ cm}^2 \text{ s}^{-1}$. The value of the diffusion coefficient of copper at 600 °C found by extrapolation is estimated at $\sim 6 - 9 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$. The bulkier Ba^{2+} ion has a lower coefficient of self-diffusion in the same temperature range ($\sim 10^{-14} - 5 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1}$).¹³⁷⁻¹³⁹ The coefficient of self-diffusion of Y^{3+} ion in the Y123-phase varies from 10^{-14} to

$10^{-16} \text{ cm}^2 \text{ s}^{-1}$ in the temperature interval 780–980 °C (the activation energy is 280 kJ mol^{-1}).¹³⁷⁻¹³⁹

Therefore, self-diffusion of oxygen in high-temperature superconducting phases proceeds at a rate which is 1–3 orders of magnitude higher than that of self-diffusion of cations, especially in those regions where low-temperature oxidation of superconductors occurs. This is first of all due to the differences in the atomic weights of the elements, the charge of their ions and structural features of high-temperature superconducting phases containing oxygen-deficient perovskite-like blocks. Taking into account different values of diffusion coefficients, the cationic framework can be considered virtually immobile when studying various low-temperature processes with participation of high-temperature superconducting phases (see also Section III.1.b and S.3).

The final stage of preparation of HTSC can be optimised using the data on the equilibrium oxygen content and the parameters of its diffusion in high-temperature superconducting phases (see above). In combination with specific features of phase relations described above, this opens additional opportunities of targeted design of high-temperature superconducting materials.

IV. Development of advanced methods for the synthesis of high-temperature superconducting materials

Preparation of high-temperature superconducting materials with desired characteristics is the most important problem that became topical immediately after the discovery of this class of complex cuprates. However, only a few types of high-temperature superconducting materials such as highly homogeneous powders (used as intermediate products for the preparation of ceramics, coatings, silver-sheathed tapes), thin films and hetero-structures, large-grain ceramics and long-length composites can be used in such areas as power engineering, electronics and medicine. A general view of the main classes of materials based on HTSC-phases is shown in Figs 19–21 (see S.8–S.10)

1. Chemical homogenisation and preparation of high-quality powders

Early studies of high-temperature superconducting materials were carried out using the so-called ceramic method, which includes thorough mechanical mixing of oxides (in some instances,

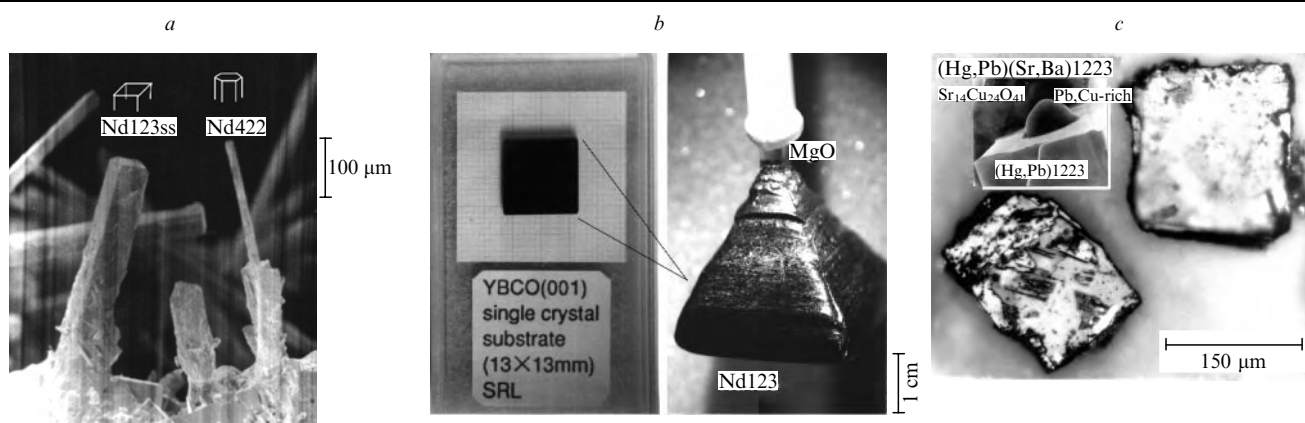


Figure 19. Single crystals of HTSC;

(a), general view of needle-shaped $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ ‘stalactic’ crystals grown under isothermal conditions by the ‘pellet-in-pellet’ method with addition of a small amount of BaF_2 (see S.8); (b) the largest (by the date of publication of this review) ‘pyramidal’ $\text{NdBa}_2\text{Cu}_3\text{O}_z$ HTSC-crystal grown by the modified Czochralski method and a polished experimental substrate for thin film deposition, obtained by sawing a ‘bulk’ $\text{YBa}_2\text{Cu}_3\text{O}_z$ crystal grown by using this method (published by courtesy of Professor Y Shiohara, SRL, ISTECH, Japan);¹¹⁴ (c) general view of plate-like mercury-containing HTSC-crystals obtained by ampoule synthesis using the contact pair method (the only Hg-based crystals with peak effect known to date, see S.9); a pronounced peak effect observed on the ‘critical current vs. external magnetic field’ dependence is assumed to be due to double (Hg/Pb and Ba/Sr) substitution (published by courtesy of S R Lee, M V Lomonosov Moscow State University, Russian Federation).

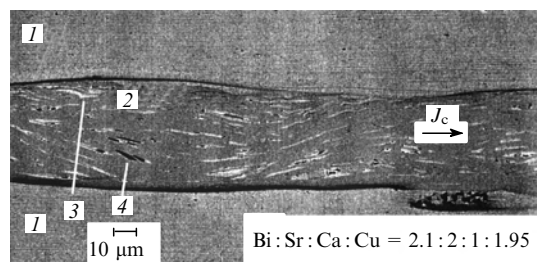


Figure 20. A SEM graph of a cross section of a long-length HTSC-composite (a silver-sheathed tape fabricated by the 'powder-in-tube' method) with optimised composition of the superconducting core; (1) silver sheath; (2) phase of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ type; (3) inclusions of particles of Ca–Sr bismuthates; (4) inclusions of particles of Ca–Sr cuprates; J_c denotes the direction of current in the superconducting wire (published by courtesy of Professor E Hellstrom, ASC, UWM, USA).⁵⁴

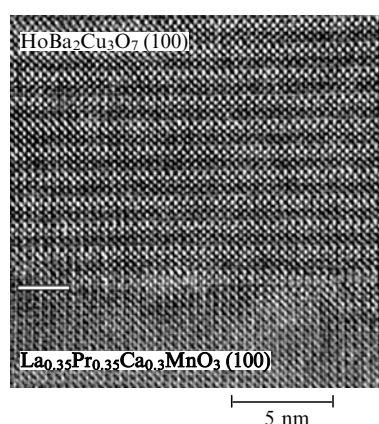


Figure 21. A cross section of $\text{HoBa}_2\text{Cu}_3\text{O}_7/(\text{La}, \text{Pr}, \text{Ca})\text{MnO}_3$ epitaxial film grown on the LaAlO_3 substrate (the 001 orientation) in the region of the HTSC–manganite interface according to high-resolution transmission electron microscopy data (see S.10). The smooth atomic layers at the interface indicate chemical compatibility of HTSC cuprate and manganite with giant magnetoresistance effect (published by courtesy of Professor A R Kaul, M V Lomonosov Moscow State University, Russian Federation).

alkaline-earth metal oxides and carbonates) and repeated 'calcination–grinding' (heat-and-heat) cycles needed for the solid-phase reaction between the reagents to proceed.^{2–5, 14}

This conventional method for the preparation of many types of structural and functional ceramics has essential drawbacks, the most important of which consists in long-term heat treatment because of rather large grain size and mixing inhomogeneity of the reagents (see S.11). Often, the growth of crystallites is uncontrollable, which results in both chemical and granulometric inhomogeneity. In combination with anisotropy of crystallites constituting the HTSC, this results in irreproducibility of their electrical and magnetic properties. Almost all oxide superconductors known to date are complex multicomponent chemical compounds. Distinctions in properties of the elements constituting high-temperature superconducting phases due to their different positions in the Periodic Table preclude development of a unified procedure for the preparation of HTSC by the ceramic method.

Publications concerning the development and application of the so-called chemical methods for the preparation of HTSC powder have been known since 1987.^{162–172} These methods allow improvement of the product homogeneity owing to the achievement of a nearly molecular level of component mixing in solution and its retention to a greater or lesser extent in subsequent stages of the synthesis. As a rule, the oxide powders thus obtained are

characterised by a rather large specific surface and, as a consequence, readily enter into solid-phase reactions and are active in sintering. Additionally, the efficiency of chemical methods of synthesis is also manifested in increased chemical homogeneity of ceramics.¹⁴

It is also appropriate to use chemical methods along with the most widely used melt solidification methods for the preparation of ceramics despite marked levelling of distinctions in the morphology of powders with different prehistory, because of complete or partial melting. The establishment of the nature of pinning centres requires materials with strictly specified content and distribution of impurities. The easiest way of doing this is to use chemical methods. Mention has been made^{9, 129, 173} of the possibility of controlling the size of crystallites of the secondary phases through the so-called effect of topochemical memory observed when varying the chemical prehistory of specimens.^{39, 40} Of particular importance is preparation of high-quality, highly disperse 'soft' powders for fabrication of long-length HTSC–metal composites (e.g., silver-sheathed tapes) by the 'powder-in-tube' method.^{16, 23, 54, 55} The size of internal cross sections of such composites varies from several to several tens micrometres. Therefore, 'coarse' and inhomogeneous powders (with broad distribution of the particle size) prepared by conventional ceramic method are unusable in this case.

The coprecipitation methods are widely used for the preparation of various types of ceramics. Therefore, it is not surprising that they were among the first chemical methods for the synthesis of HTSC powder.^{2, 29, 162} In some instances (in correctly designed experiments) it has been possible to prepare homogeneous disperse mixtures of salts with the predetermined cation ratio and to reproduce the results obtained. In an ideal case, the conditions under which precipitation of cations from a solution occurs simultaneously and at equal rates are optimum. Most of the methods used include precipitation of carbon-containing salts (oxalates and carbonates) the thermolysis of which is completed at 900–950 °C. Unfortunately, the presence of carbon-containing salts should be considered as a drawback of this type of method because of the possibility of the formation of oxycarbonate phases.^{36, 100, 136}

The citrate method^{2, 171} is the most widely used of the different versions of the sol-gel methods. Closely related to this method is the method of polymerised complexes, which has been successfully developed in a number of research laboratories worldwide.¹⁶³ In this case, the ability of α -hydroxy acids (e.g., citric acid) to form chelate complexes with metal ions is used. When heated to 100–140 °C, such complexes react with polyfunctional alcohols (e.g., ethylene glycol) to give low-molecular-weight oligomers (esterification). Subsequent heating to 180–200 °C results in their polymerisation and the formation of a viscous resin (gel) with uniformly distributed metal atoms. The gel can be decomposed to give the oxide powder. The sol-gel method is rather simple and inexpensive since almost no complex equipment is needed (the method requires no centrifuging, filtering, washing, drying, etc.) and readily available nitrates are most often used as initial substances. The viscosity of the gel obtained can be controlled by varying the component ratio and the duration and temperature of polymerisation. Therefore, the sol-gel method is used for the preparation of not only powders, but also thick films, fibres and planar ceramics.

Currently, the spray drying and spray pyrolysis techniques have received the widest acceptance among chemical methods for preparation of HTSC powders.^{162, 172} The latter method includes sonication of a mixture of salt solutions to obtain a mist with a droplet size of 0.5–0.8 μm , the transfer by a carrier gas into a hot chamber where instantaneous (complete or partial) decomposition of the droplets occurs. The oxide-salt product that is formed is collected on a filter at the outlet of the gas flow from the decomposition zone.

The molecular level of mixing of components (most often, nitrate solutions) and nearly instantaneous dehydration and

decomposition of microscopic spray droplets make it possible to prepare a homogeneous product. Repeated grinding and calcination characteristic of the ceramic technology and responsible for contamination of the product and uncontrollable grain growth are excluded in this case. However, the powders obtained can be contaminated with the material of the drying chamber (at high temperatures, in the presence of free acid). Additionally, the spray pyrolysis technique requires careful purification of large volumes of the carrier gas (oxygen) from CO_2 to avoid the formation of barium carbonate.

The method of rapid expansion of supercritical solutions (RESS)^{169, 170} at elevated temperature and pressure is based on the phenomenon of an anomalous increase in the solubility of inorganic compounds in water (or in other solvents such as ammonia, carbon dioxide, xenon, *etc.*) above its critical temperature (in autoclave). When such solutions are expanded in a chamber at a reduced pressure and temperature, the solubilities of the solutes decrease substantially and these are isolated as ultradisperse particles (often, as an X-ray amorphous phase or metastable crystalline modifications). Oxide materials can be best prepared using aqueous supercritical solutions.¹⁶⁹

The drawbacks of most chemical methods used for the synthesis of HTSC powders can be to a great extent compensated using cryochemical technology.^{162, 165–168} This method consists in the preparation of highly disperse and highly homogeneous salt (and the oxide) precursors by fast freezing of finely disperse salt solutions (preparation of cryogranulates) followed by removal of water by sublimation. Experimental conditions should exclude physicochemical processes resulting in deterioration of chemical and granulometric homogeneity of the product, *e.g.*, separation of sprayed microscopic drops into solvent-rich and solvent-depleted regions due to insufficiently high cooling rate, partial melting of cryogranulates and, hence, segregation of the components during the freeze-drying or on subsequent heat treatment of the freeze-dried product, *etc.*

Therefore, the highest homogeneity of the product is often achieved by (i) spraying the solution over a massive metal plate cooled by liquid nitrogen,¹⁶⁸ (ii) replacing (if possible) nitrate solutions by acetate^{168, 174} or nitrate–nitrite solutions and (iii) drying in a thin layer with slow heating to 125 °C in an argon stream^{14, 168} and decomposing the dried salt product in a furnace preheated to the desired temperature.

The use of highly disperse (tens of nanometres) and highly homogeneous precursors prepared by the cryochemical method makes it possible to accelerate substantially the phase formation and to prepare high-temperature superconducting phases that can hardly be synthesised by other methods. For instance, the Bi2223-phase was obtained¹⁶⁸ after annealing for 12–16 h only (*cf.* 200–300 h required when using the ceramic technology) at 750 °C and the Y124-phase was synthesised¹⁶⁸ after annealing in air at 815 °C (120 h). In the latter case, high-pressure stages (p_{O_2} up to 100 atm) usually required to synthesise this phase were excluded. Considerable achievements have been made in the preparation of different homologues of mercury-containing HTSC by the ampoule method using cryochemical technology and other methods of chemical homogenisation.¹⁷⁵

2. Thin film preparation

The known technologies of thin film preparation can formally be divided into physical and chemical ones.^{2, 24, 176} The former comprise the most widely used methods of pulse laser deposition and magnetron sputtering of films including the transfer of the material of the dense and chemically homogeneous target in the form of microscopic clusters knocked out by a high-energy beam from the target onto a substrate. These methods make it possible to prepare high-quality thin films with record physical characteristics and to carry out a layer-by-layer synthesis of novel types of structures (structural design) by ‘assembling’ the film literally at the atomic plane level.

However, expensive physical methods are almost inapplicable for the preparation of large specimens. This is achieved by using such chemical methods as liquid phase epitaxy (LPE)^{8, 112, 120} and chemical vapour deposition (CVD).²⁴ However, despite the advantages of precipitation from a solution in a melt by LPE, this has not acquired wide acceptance to date and has been developed by only a few research groups.¹²⁰ Among accepted methods for the preparation of thin high-temperature superconducting films, deposition on single-crystal substrates of thermally decomposed products of highly volatile organometallic precursors (Metal-Organic Chemical Vapor Deposition or MOCVD) is the most interesting.

Currently, the efforts of researchers from about 40 laboratories¹⁴ including those of the biggest electronic companies are focused on the development and improvement of CVD technology for the preparation of HTSC. This fact, as well as information on large-scale applications of the CVD method for the preparation of diverse epitaxial semiconducting films and oxide coatings suggest that this method can become one of the main methods for the preparation of high-temperature superconducting films in the future.

The MOCVD method^{2, 24} includes transfer of the metal constituents of films to the reactor as vapours of volatile organometallic compounds, mixing of the vapours with a gaseous oxidant and decomposition of the vapours in a hot-wall reactor or on a heated substrate followed by the formation of a HTSC film. Metal β -diketonates are most often used as volatile compounds (precursors). Novel volatile organometallic compounds^{2, 24, 177–179} made it possible to improve substantially film characteristics and to extend the potentialities of the MOCVD method.

The MOCVD method makes it possible to prepare thin HTSC films with characteristics that are at least as good as those of films prepared by physical methods. The obvious advantages of this method include first of all its versatility as regards the composition of the materials obtained, the possibility of single- and double-sided deposition of films with homogeneous composition and the same thickness on substrates with complex shapes and large surface areas (including continuous film deposition on a long-length metallic substrate, *e.g.*, a tape).¹⁷⁶ Unlike physical methods of sputtering, in which high performance of equipment is achieved due to the high energy of the particle beam of the sputtered substance and is connected with the risk of disturbing the morphology and stoichiometry of the film thus formed, the performance of the MOCVD method is achieved by increasing the vapour pressure of the volatile component and/or by increasing the flow rate of the carrier gas. Other advantages of the MOCVD method are the possibility of achieving higher deposition rates (up to several millimetres per hour) with retention of high quality of the film, the use of a flow-through setup operating at pressures of 10^{-3} –1 atm instead of high-vacuum equipment, its simplicity and low cost compared to those required when using physical methods and, finally, ‘flexibility’ of the process in the adjustment stage (primarily due to the smooth change in the vapour phase composition).

A common problem of all methods of thin film preparation including the MOCVD method is ‘symbiotic’ choice of substrates. The substrates should be highly chemically inert (to prevent contamination of high-temperature superconducting phase with alien components), cheap and readily available. Additionally, the substrate material must possess specific physical properties such as (i) rather small (< 2%) mismatch between the crystal lattice parameters and those of the deposited film to provide conditions for the epitaxial growth, (ii) close values of the thermal expansion coefficients (TEC) of the substrate and HTSC phase to avoid the formation of microscopic cracks in the film due to compression and, especially, tension caused by temperature variations; (iii) the absence of twinning-type phase transitions that can appreciably deteriorate the film morphology and (iv) low dielectric constant and dielectric loss tangent to provide the possibility of using the films in microelectronics and in microwave devices.

Unfortunately, almost none of the known substrates meets all the above-mentioned requirements (Fig. 22). Usually, SrTiO_3 , NdGaO_3 and LaAlO_3 are used as substrates.¹⁷⁹ Recently, large Y123 and Nd123 single crystals were used for homoepitaxy of the R123-phases of high-temperature superconducting films.¹⁸⁰ However, these single-crystal substrates are superconductors rather than dielectrics. Intrinsic in these substrates is the tetragonal-to-orthorhombic phase transition (*tetra-ortho*-transition) accompanied by the formation of a twin structure. Non-superconducting tetragonal solid solutions of the $\text{Pr}_{1-x}\text{Ba}_x\text{Cu}_3\text{O}_z$ type, in which no twinning occurs, seem to be more promising.⁸ Dielectric $\text{Nd}_{1.85}\text{Ba}_{1.15}\text{Cu}_3\text{O}_z$ single crystals are characterised by a high degree of orthorhombicity, the absence of *tetra-ortho*-transition, close TEC values, high lattice parameter matching with high-temperature superconducting films of the R123-phases and a narrow range of oxygen nonstoichiometry. For these reasons, they are also promising for use as substrates.^{80, 81, 181}

The second, chemical problem arising when using the MOCVO method is the control of the cation and anion stoichiometry of the films. The chemical vapour deposition is an incongruent process and depends on several factors such as the temperature, total pressure, partial pressures of oxygen, carbon dioxide and water (the oxidation products of the organic component of compounds used), their flow rates and distribution of the flows in the reactor and above the substrate, total composition and homogeneity of mixing of volatile components in the gas phase, *etc.* The most promising way of controlling the vapour composition is to carry out instantaneous evaporation of the mixture of volatile components from one source. This is achieved by using an aerosol obtained from the solution of organometallic compounds in organic solvent (*e.g.*, diglyme) or by pulse evaporation of microscopic portions of a mixture of organometallic compounds fed using a belt-conveyor feeder.²⁴

In the first case, the solvent vapour has a strong effect on the film deposition, namely, the thermal effect of solvent oxidation: a decrease in the partial pressure of oxygen and an increase in the partial pressure of carbon dioxide and water are observed. Using the results of thermodynamic analysis, it is possible to minimise the influence of these effects and to optimise the conditions for film deposition in the reactor with cold walls and induction heating of the substrate.^{2, 24, 179} At $p_{\text{CO}_2} < 10^{-5}$ atm and $T < 800$ °C, no barriers to the formation of the $\text{YBa}_2\text{Cu}_3\text{O}_{z-}$

phase are observed. Using an aerosol source, it is possible to attain high deposition rates and reproducibility of the composition and morphology of the R123- and Bi2212-films.¹⁷⁷

The second method consists in placing small droplets of an organic solution containing volatile metal complexes in a predetermined ratio on a fibre glass transport tape. The vapour formed on pulse heating of the tape in a vacuum chamber moves to the substrate. The amount of substances evaporated per pulse as well as the vapour composition can easily be varied from pulse to pulse. This method appeared to be very useful in the preparation of multilayered film structures of complex chemical composition.^{182, 183}

The third problem that arises only when using the MOCVD method consists in the necessity of a targeted search for highly volatile substances with reproducible volatility. The most serious problems are associated with barium transfer through the vapour phase. Because of coordinative unsaturation of Ba^{2+} ions and high ionicity of the barium–oxygen bond, barium complexes are oligomerised in both the solid and vapour phases. Stabilisation of barium dipivaloylmethanate is achieved by using the adduct of dipivaloylmethanate with phenanthroline, which saturates the coordination sphere of barium, thus resulting in nearly quantitative transition of this complex to the vapour phase.^{2, 24}

The fourth (technological) problem is associated with the necessity of designing the optimum film morphology. It was shown in the studies of the effect of various factors on the orientation of films that the introduction of an excess of bismuth and copper compounds in the course of growth of high-temperature superconducting Bi2212-films favours the formation of *c*-oriented films, whereas the introduction of an excess of an alkaline-earth metal results in *a*-oriented films.¹⁷⁷ This is associated with the fact that the presence of the excess of bismuth and copper results in the formation of an equilibrium liquid phase or, at least, in a shift of the compositional point towards the regions where a melt should be present. This increases the mobility of the film components and facilitates the formation of thermodynamically more favourable *c*-oriented films, whereas *a*-oriented films are formed under kinetically controlled conditions. This is confirmed by the LPE experiments.¹²⁰ Generally, the morphology (polycrystallinity, planarity, film orientation, the presence of microscopic inclusions of non-superconducting phases, microscopic cracks, *etc.*) depends on numerous process factors that should be optimised thoroughly.

The most topical problems associated with the development of the MOCVD technology and requiring practical solution are connected with deposition of $\text{RBA}_2\text{Cu}_3\text{O}_z$ -films on bicrystalline substrates (SrTiO_3 , sapphire) and fabrication of devices based on the Josephson effect (logistors, SQUID magnetometers, *etc.*), preparation of high-temperature superconducting films using substrates with a large surface area (up to 70 mm in diameter), *in situ* double-sided deposition of films and attainment of high superconduction characteristics of thin high-temperature superconducting films using conventional substrates (R-sapphire, Si) and high-quality CeO_2 buffer layer.¹⁸⁴

Recently, R123-films (R is the 'light' RE element), the effects of stabilisation of metastable phases (see S.11) and an increase in the critical currents in solid solutions have attracted the attention of researchers. Yet another topical problem is the preparation of thick films with high current-carrying ability deposited on flexible tapes made of nickel metal and its alloys (the so-called 'Rolling-Assistant Biaxially Textured Substrates' or RABiTS) preliminarily coated with a buffer layer.¹⁷⁶ The CVD method is certain to play a key role in solving this problem.

3. Large-grain ceramics and single crystals

a. Characteristic features of materials based on large-grain ceramics

Real structure. As a rule, the idea of designing any material is based on a concept of a real structure with several hierarchical levels.^{185, 186} The basic crystal structure determines the fundamen-

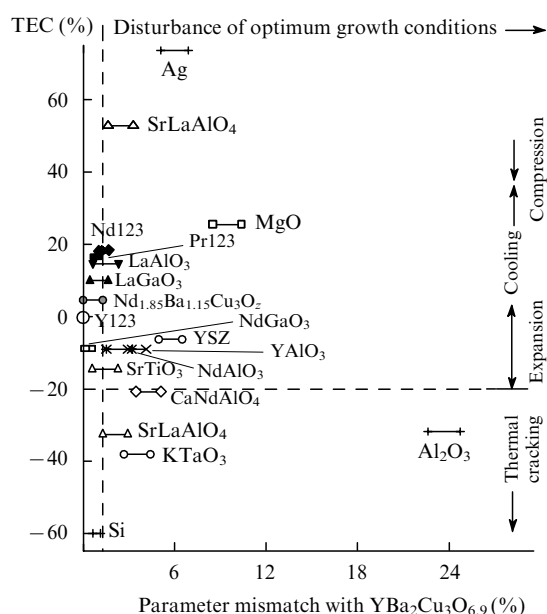


Figure 22. Properties of materials used as substrates for the deposition of high-temperature superconducting thin films.

tal properties of HTSC and is responsible for their structural organisation at the microscopic level. Individual crystallites, which are always imperfect and consist usually of smaller subcrystallites (mosaic blocks, coherent scattering domains) separated by extended defects, form an intermediate (mesoscopic) level. Ensembles of crystallites (grains, granules) and pores form the macroscopic level of structural organisation of HTSC. The current concepts on complicated structure of melt-processed specimens of superconducting ceramics are illustrated in Fig. 23.^{9, 11, 55, 187–191}

Ensembles of large pseudo-single-crystal domains (their size reaches 0.5–5 cm depending on the precipitation conditions) separated by large-angle boundaries are the main microstructural motifs of large-grain ceramics. Each domain is a stack of thin (5–50 μm) $\text{RBa}_2\text{Cu}_3\text{O}_x$ -plates or lamellae rather than a true single crystal. The lamellae are characterised by the aspect ratio of ~ 1000 . The plates are oriented parallel to one another and separated by low-angle boundaries, which makes them ‘transparent’ to the critical current. It should be noted that the real structure of melt-processed HTSC is characterised by the presence of various extended defects such as twin boundaries, ultradisperse inclusions of non-superconducting phases, different types of microscopic and macroscopic cracks, appeared due to low plasticity of the $\text{RBa}_2\text{Cu}_3\text{O}_x$ -phase, and increased concentration of dislocations. In principle, all levels of structural organisation of HTSC should be taken into account. However, only the composition, structure of boundaries and nature of various defects have been studied in detail,^{187–191} though such parameters as porosity and density of ceramics as well as the size of crystallites and pores should also be considered.

The real structure of melt-processed HTSC can be considered as a large-domain system with pronounced ‘collective’ superconducting properties resulting in very high integral superconductivity characteristics due to the specific crystallisation mechanism of the peritectic melt.^{9, 11} For instance, an increase in the total density of specimens as a result of melt solidification eliminates the percolation problems characteristic of the current flow in the specimens obtained by solid-phase synthesis. ‘Pseudo-single-crystalline domains’ are united to form macroscopic aggregates that (potentially) can carry heavy critical currents. Finally, a large number of structural defects (inclusions, dislocations, low-angle boundaries) favours the appearance of new pinning centres.⁶ Unfortunately, only the ‘lamellar’ level of the structure of melt-processed materials is formed spontaneously and is characterised by high superconducting parameters. The remaining hierarchical levels of the structure can be formed only by using special techniques.

Methods of generation of new pinning centres. Generation of efficient pinning centres of the magnetic flux, which make it possible to increase substantially the critical current density J_c inside the grains, is the most important stage of the preparation of materials with a high repulsion force. The methods of solving this problem can arbitrarily be divided into physical and chemical ones.

Currently, the highest J_c values have been obtained using samples of superconducting ceramics irradiated with high-energy particles. Irradiation of samples with neutrons or heavy ions to produce cluster-type radiation defects (tracks) of size 20–100 nm was found to be the most efficient.^{192, 193} In this case, the J_c value increases in proportion to the irradiation dose. However, this type of treatment encounters considerable technological difficulties. Additionally, it has such drawbacks as residual activity of materials and the possibility of radiation-induced degradation of samples if the radiation doses exceed an optimum.

More promising are chemical methods which make it possible to introduce non-superconducting highly disperse inclusions in the matrix of the 123-phase.^{194–203} Particles of the Y_2BaCuO_5 -phase, an intermediate crystallisation product, are most often used as inclusions.^{194–197} The results obtained in the studies of pinning^{6, 9, 11} suggest that changes in J_c depend on the content and

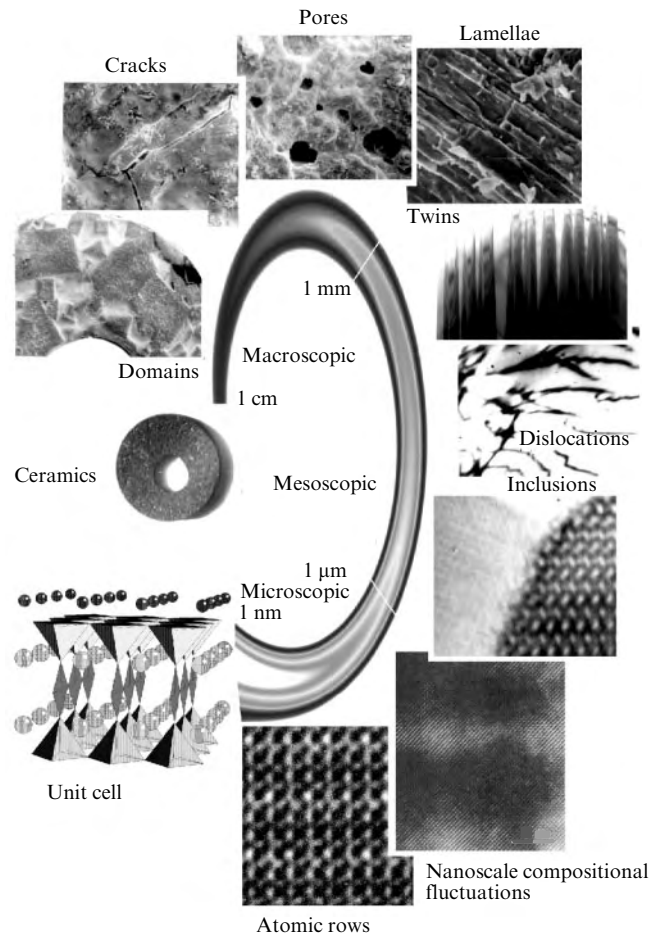


Figure 23. Macroscopic (10^{-3} – 10^{-2} m), mesoscopic (10^{-6} – 10^{-3} m) and microscopic (10^{-10} – 10^{-6} m) levels of real structure of large-grain ceramics.

dispersity of the Y_2BaCuO_5 -phase. It is noteworthy that particles of this phase are not the pinning centres themselves and that the major contribution is made by the 123-phase–211-phase interface and the interfacial defects. Introduction of zirconates, titanates, stannates, nickel metal, uranium-235 oxide (its radioactive decay leads to ‘internal’ irradiation of the superconducting matrix) also results in generation of new pinning centres (see Fig. 4).

Types of intercrystallite boundaries. Generation of efficient pinning centres plays an important role in the preparation of high-temperature superconducting materials characterised by high values of the transport critical currents. However, in this case the perfection of intercrystallite boundaries and their ‘transparency’ to the critical current are the most important points. As has been mentioned above, the oxide superconductors are characterised by abnormally low coherence lengths (ξ). Because of this, two types of links are formed between the crystallites, *viz.*, strong links (ordinary intergrain phase contacts similar to intercrystallite ‘necks’) and weak links which, in the general case, are the breaks of the phase continuity. The extension of weak links is comparable with ξ values. The reasons for the phase discontinuity can be the formation of both the domains with local changes in stoichiometry and amorphous domains on intercrystallite boundaries, or the appearance of microscopic cracks, as well as high crystallographic anisotropy of HTSC and spatial disordering of crystallites.^{204–206}

In accordance with the formation mechanism of the 123-phase, the ensemble of growing crystallites formed in the early stages of melt crystallisation consists of *c*-oriented nuclei with disordered orientations in the *ab* plane. Growth of particles of such

an ensemble and their coalescence result in the formation of large-angle boundaries that are parallel to the c axis and the tilt boundaries that are perpendicular to the c axis. The best transport characteristics will be obtained if the current will flow through both types of boundaries without a considerable loss. Based on these grounds, a 'brick wall' model of the transport current flow through high-temperature superconducting materials was proposed.²⁰⁷ According to this model, the tilt boundaries enabling the maximum surface area of intercrystallite contacts play an important role in the formation of high transport current.

However, the 'brick wall' model does not consider the current flow through large-angle boundaries along the ab plane. According to the 'railway switch' model,²⁰⁸ there are both large-angle intergrain boundaries and a rather large relative amount of intercrystallite links 'transparent' to the current flow, which favours low current loss. These links responsible for the current flow through intercrystallite boundaries and the current flow through the tilt boundaries necessary for obtaining the maximum surface area of intercrystallite contacts form a three-dimensional superconducting network. Such a mechanism is most characteristic of bismuth-containing HTSC. Probably, it can also be postulated for yttrium-containing polycrystalline superconductors.

Thus, the density of the critical current that flows through intercrystallite boundaries is mainly determined by mutual spatial orientation of their constituent crystallites. Nevertheless, it was assumed²⁰⁹ that in the general case the J_c values are only dependent on the surface area of the 'strongly linked' areas of intercrystallite boundary. Obviously, the probability for two oriented (textured) crystallites to be 'strongly linked' is much higher than for disordered grains. However, it was reported²⁰⁹ that high J_c values can also be retained in the latter (unfavourable) case. The results of recent studies^{176, 210} indicate the presence of high-angle-but-low-energy (HABLE) boundaries, thus confirming this conclusion. This means that probability factors come into play when considering the problem of a critical transport current in bulk specimens.^{9, 55, 128, 129}

b. Methods of preparation

Large-grain ceramics cannot be a chemically and structurally homogeneous material. It is a composite whose practically important superconducting properties are superior to those of

highly homogeneous specimens and single crystals. Therefore, the development of melt solidification processes revolutionised the production technology of high-temperature superconducting ceramics since it opened a new way to the practical use of superconducting ceramic materials.

Minimisation of the inclusion size of secondary phases. The modern classification of melt solidification procedures for preparation of HTSC and the most important details including the chemical type of the starting precursor, mechanical prehistory and the heat treatment regime are presented in Fig. 24. Some trends in the development of melt solidification methods can be traced, which made possible the preparation of materials with high superconducting characteristics. These are:⁷⁻¹¹

- (1) a step-by-step change in the regime of high-temperature treatment in order to increase the degree of nonequilibrium in all stages of the process;
- (2) the use of methods of synthesis resulting in more homogeneous and disperse starting oxide powders;
- (3) the use of precursors in different initial states and the introduction of various additives.

The first trend is associated mainly with attempts to shorten the duration of treatment of samples at maximum temperatures. This made it possible to prevent the rapid growth of particles of secondary phases at temperatures above the peritectic temperature, which was probably a reason for passing from the classical 'Melt-Textured-Growth' (MTG) method to its modified version, viz., 'Liquid Phase Processing' (LPP).

The 'Quenched-Melt-Growth' (QMG) method involves a chemically induced increase in the degree of nonequilibrium of the system. In this case, the 211-phase is formed in the region of thermodynamic stability as a result of a fast 'downward' interaction of Y_2O_3 with the melt rather than due to relatively slow 'upward' decomposition of $YBa_2Cu_3O_7$. Experiments on super-fast cooling of droplets of a high-temperature $Y_2O_3 + L$ melt in an evacuated vertical metallic tube²¹¹ are probably one of the most successful implementations of this method.

The QMG method has an important alternative, the doping of melts with, e.g., platinum²¹² (the 'Platinum-Doped-Melt-Growth' or PDMG technique) and cerium dioxide.²¹³ In this case, the formation and decomposition of not-too-stable Pt-containing complex oxides ($Ba_4CuPt_2O_9$, $R_2Ba_2CuPt_2O_8$, $R_2Ba_3Cu_2PtO_{10}$, etc.) not only affects the nucleation processes,

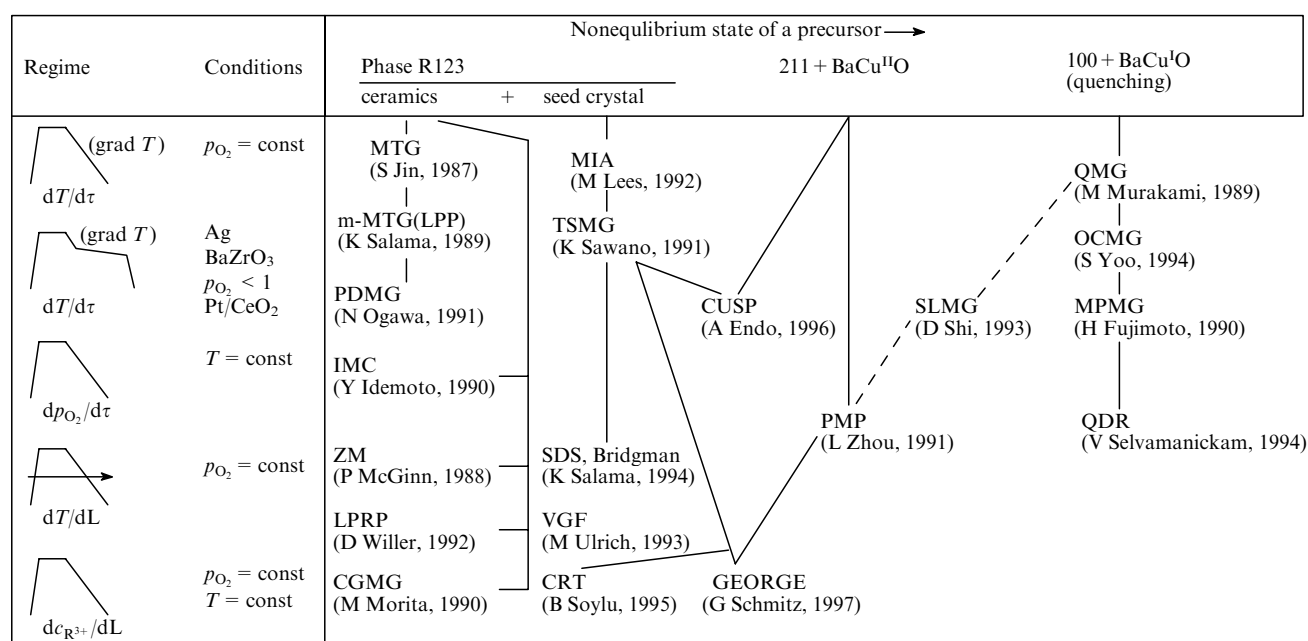


Figure 24. Melt solidification methods of preparation of large-grain ceramics.

but also retards the growth of individual faces of crystallites of the 211-phase. This results in a change in their shapes and sizes and prevents coalescence of the crystallites into larger aggregates.²¹³

Several methods such as the 'Melt-Powder-Melt-Growth' (MPMG) and 'Powder-Melt-Process' (PMP) involve additional grinding of both the starting reagents and intermediate products in order to increase their dispersity and homogeneity of mixing.^{6, 214} A successful attempt has been performed at using a highly homogeneous mixture of barium cuprate and copper oxide with yttrium oxide, which simulates the phase composition of the specimens prepared by the QMG method (the so-called 'Solid-Liquid-Melt-Growth', or SLMG method).¹⁹⁷ Yet another, basically new modification of this method is the directional recrystallisation of amorphised quenched melt at temperatures $\sim 100^\circ\text{C}$ below the peritectic decomposition temperature of the 123-phase (the so-called 'Quench-and-Directional-Recrystallisation' or QDR method). This allows a rather fast (over 3–5 min) formation of the 123-phase and ultradisperse 'green' phase and preparation of highly textured superconducting ceramics using conventional zone melting technique with reduced hot zone temperature.²¹⁵

A positive effect of the above-mentioned innovations becomes more understandable when considering numerous experimental data indicating that the particle size of the 211-phase depends on prehistory of the system, despite the extreme conditions for the synthesis.^{9, 173, 216, 217} This is probably due to the possibility of intermediate formation of a superheated metastable (congruent) melt of the 123-phase. Numerous structural defects (grain boundaries mostly) accumulated mainly in the fine crystalline material facilitate strongly the decomposition of the congruent melt into a melt and the 211-phase. However, the excess 'green' phase can inhibit the growth of faces of the 123-phase on sintering, thus resulting in a more fine-grained structure.²¹⁷ The addition of Pt or CeO_2 changes the surface energy at the 211-phase–melt interface and results in the formation of the 211-phase with another morphology (needle-shaped particles). In accordance with the mechanism considered above, this facilitates dispersion of anisotropic particles of the 211-phase by the moving crystallisation front and, finally, the formation of more finely disperse inclusions of the 211-phase in the 123-phase matrix (see Table 3). The possibility of controlling the composition of composites by extracting the excess of BaCuO_2 from stoichiometric specimens of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ -phase using porous Y_2BaCuO_5 -substrates (the so-called 'Liquid-Phase-Removal-Process' or LPRP method) was also reported.²⁰⁰

Thus, the analysis of the published data^{9, 11, 55} shows that an increase in the dispersity and uniformity of distribution of the particles of secondary phases is simultaneously one of the major lines of modification of the 'melt solidification processes' and a criterion for evolution of these methods. The 211-phase has a complex effect on the microstructural and functional characteristics of specimens. This phase is responsible for completeness of crystallisation, strength of materials, morphology of the superconductor grains and the appearance of new pinning centres. Eventually, controllable modification and variation of the above-mentioned processes and parameters results in an essential improvement of functional characteristics of the materials obtained.

The role of gas atmosphere. As has been mentioned above, gas exchange with the environment plays an essential role in the preparation of high-temperature superconducting materials. By varying the partial pressure of oxygen it is possible to solve several important problems. First is the problem of reduction of the crystallisation temperature and provision of compatibility of the melt with low-melting substrates. The second problem is associated with modification of procedures for creation of supersaturation by smooth variation of the partial pressure of oxygen, which can favour both controllability of the process and a decrease in the amount of impurities in the final product. Third, prevention of bubbling and deformation of melt-processed material. Finally, the

fourth problem is the control of both the width of the homogeneity region and the cation ordering in the solid solutions based on the 123-phase.

The effect of partial pressure of oxygen on the processes of preparation of high-temperature superconducting materials has been little studied.^{13, 218–222} A decrease in the temperature of peritectic melting of the 123-phase at reduced oxygen content and the formation of low-melting eutectics²²⁰ containing Cu(I) (at $770–800^\circ\text{C}$) was observed.^{218, 219} This made it possible to lower the growth temperature of single crystals of the 123-phase (down to $\sim 910^\circ\text{C}$ at $p_{\text{O}_2} = 5 \times 10^2–2 \times 10^4 \text{ Pa}$)²²⁰ and to prepare thick films on a silver substrate [$T_m(\text{Ag}) \approx 960^\circ\text{C}$] as well as rather dense bulky polycrystalline specimens.^{13, 221, 222} An original synthetic method consisting of isothermal crystallisation accompanied by a slow increase in the partial pressure of oxygen has been reported.^{218, 220} In this case, the process begins at a low partial pressure of oxygen and is completed in pure oxygen (the so-called 'Isothermal Melt Crystallisation' of IMC method).

Obviously, the density of superconducting materials should be maximum. However, the specimens prepared by melt solidification processes change their linear dimensions and shapes during oxygen exchange,^{9, 11, 55, 129} which results in an increase in their volumes and in the formation of a well-developed pore system which can hardly be removed. This problem is usually considered as applied to bismuth-containing high-temperature superconducting silver-sheathed tapes.²³ Unfortunately, almost no studies on this effect in high-temperature superconducting R–Ba–Cu–O materials have been reported, though it also plays a negative role, especially in the fabrication of materials with high critical transport currents. Experiments have shown that the main factors affecting the oxygen exchange between a sample and a gas phase are the phase composition, chemical homogeneity, relative content of Cu(I) in the solid phase, partial pressure of oxygen and the procedure used for compacting the sample.^{9, 129}

Currently, the 123-phases containing 'light' RE metals (La, Nd, Sm and Eu) are often synthesised using the single-crystal growth and preparation of melt-processed ceramics in an inert atmosphere. This is first of all due to the necessity of decreasing the degree of REE substitution for Ba in solid solutions in order to increase the transition temperature to the superconducting state.^{7, 8}

Formation of single-domain structure. Taking into account the grain boundary models considered above, it can be assumed that the most favourable way of fabricating the HTSC capable of carrying strong critical transport currents is to prepare textured materials.^{223–231} Attempts at preparing superconducting ceramics with oriented (plate- or rod-like) structure were based on conventional texturing procedures such as slow cooling in a uniform temperature field ($\text{grad } T = 0$), slow cooling in a temperature gradient field ($\text{grad } T > 0$) without moving a specimen (versions of the Bridgman method: 'Vertical Gradient Freezing' or VGF, 'Seeded Directional Solidification' or SDS), a gradient crystallisation with a moving hot zone (the 'Zone Melting' or ZM method) and the use of seed crystals (the 'Top-Seeded-Melt-Growth' or TSMG method). Non-traditional methods, *e.g.*, crystallisation along the concentration gradient (the so-called 'Constitutional-Gradient-Melt-Growth' (CGMG) and 'Geometrically-Organised-Growth-Evaluation' (GEORGE) processes) are also used.

Introduction of artificial nucleation centres of the 123-phase is an efficient method for controlling the nucleation. Such centres are formed by introducing relatively large seed crystals of REE-containing analogues of the 123-phase with higher peritectic decomposition temperature.²²³ Usually, Sm123 ($T_p \approx 1050^\circ\text{C}$) and Nd123 ($T_p \approx 1085^\circ\text{C}$) phases are used as seed crystals. As a rule, the seed crystals are placed on top of a dense substrate (a pellet or a rod). Then the melt–crystallisation cycle is performed using the temperature gradient or movement of the hot zone along the sample. The seed crystal with higher melting temperature initiates the growth of the desired phase along the direction of

propagation of the crystallisation front, which results in the formation of giant pseudo-single-crystal domains whose dimensions are comparable with those of the sample.^{7, 8, 224–226}

It is noteworthy that the orientation of pseudo-single crystals thus formed virtually coincides with that of the seed crystal, therefore the growth direction of the 123-phase is readily controllable. This is probably due to the epitaxial character of the process on the faces of the seed crystal, the unit cell parameters of which are close to those of the desired 123-phase. Often, the observed formation of differently oriented domains indicates complexity of the actual growth mechanism.⁸ It was proposed to coat the 'non-working' surface of the seed-crystallising specimens with compounds that form the Yb123-phase with a lower peritectic decomposition temperature, thus preventing crystallisation on the lateral surface of the pellet.²²⁵ Single crystals of magnesium oxide and strontium titanate were also proposed as seed crystals; however, no epitaxy was observed because of the chemical reaction between the melt and seed crystals and the formation of a buffer layer of the reaction products, so the efficiency of using such seed crystals decreases drastically.^{6, 7}

If the seed crystals are introduced at the beginning of melt crystallisation in the course of its cooling, it is possible to obtain large-grain specimens of high quality. The 'Constant-Undercooling-Solidification-Processing' (CUSP) method,^{8, 226} consisting in isothermal crystallisation of the 123-phase after introduction of a seed crystal into the hot zone, is a modification of the above-mentioned approach. Unfortunately, it is difficult to introduce a large number of oriented seed crystals anisotropically distributed in the bulk of the sample, which is necessary for the corresponding texturing of a high-temperature superconducting material (the 'Composite Reaction Texturing' or CRT method).²²⁷ Only a few studies concerning the introduction of multiple seed crystals either into the bulk or on the surface of specimens have been reported so far.²²⁸

Magnetically induced alignment (MIA)^{229, 230} is performed using REE atoms with large magnetic moments (Gd, Dy and Ho). The degree of magnetically induced texturing of the specimens prepared even by ordinary sintering increases in proportion to the applied magnetic field. Combination of this approach with crystallisation from the melt increases its efficiency, which reaches an optimum value in magnetic fields higher than 1 T.²³⁰

Mention should be made of the original CGMG method in which crystallisation is driven by the gradient of the REE concentration in the melt, resulting from varying the concentration of REE (e.g., Yb and Y) with different peritectic decomposition temperatures.²³¹ It is believed that this method can serve as a basis for the development of a process of preparation of long-length textured materials including tapes sheathed with highly oriented 123-phase.²²⁸

Chemical modification and generation of efficient pinning centres. The 'Oxygen-Controlled-Melt-Growth' (OCMG) method is a new method for the preparation of high-temperature superconducting materials at reduced partial pressure of oxygen (0.1 mol. %–1 mol. % O₂).^{7, 232} It is based on the ability of REE with the largest ionic radii (in particular, Nd, Sm, Eu and Gd) to form solid solutions of the R_{1+x}Ba_{2-x}Cu₃O_z type. Crystallisation from the melt at reduced partial pressure of oxygen results in a considerable decrease in the degree of barium substitution and in appreciable increase in the transition temperature to the superconducting state (up to 95–96 K).^{7, 8, 76, 86, 88} This is also connected⁸⁸ with possible cation ordering in the crystal lattice, e.g., with the formation of pairs of neodymium ions in the barium positions, which results in the ordering of the oxygen sublattice. At the same time, domains with fluctuations of chemical composition can appear in such a superconducting matrix. These domains are efficient pinning centres because of the strong suppression of superconductivity therein in nonzero magnetic fields, which results in the peak effect (see Fig. 4).^{7, 8}

The advantage of the pinning centres thus generated over point defects consists in higher efficiency of modulations of

chemical composition of the structure at relatively high temperatures (the liquid nitrogen temperature) corresponding to the operating mode of high-temperature superconducting materials. The formation of these types of pinning centres that were not observed for the Y123-phases is the major advantage of the OCMG method, which allows the preparation of superconducting materials with record characteristics.⁷

Several reasons for the appearance of pinning centres are discussed in different models.^{7, 8, 76, 232–234} The first of them is connected with random fluctuations of the Nd:Ba ratio in the superconducting matrix due to local fluctuations of temperature, *p*O₂ and the melt composition during the growth of the pseudo-single-crystal domains (for the OCMG method). The next reason is the formation of a quasi-ordered nanostructure as a result of spinodal decomposition of the solid solution caused by post-crystallisation annealing. Third, it is the formation of clusters, oxygen vacancies and twin boundaries in the case of nonuniform oxygen distribution in the superconducting matrix. Next, the pinning centres can appear due to the formation of highly disperse inclusions of the R422-phases and redistribution of cations between the matrix and these non-superconducting inclusions. Finally, antistructural defects produced in the course of (probable) mutual exchange of Nd³⁺ and Ba²⁺ ions between the corresponding crystallographic positions can also result in the appearance of pinning centres (see S.12).

The peak effect observed in all R123-phases including R = Y is associated with the presence of local oxygen-deficient regions characterised by lower *T*_c as compared to that of the entire matrix.^{233, 234} It is assumed²³³ that this effect increases due to the presence of impurities (e.g., the components of the crucible) which reduce the oxygen mobility and favour its nonuniform distribution. It was hypothesised⁹³ that nonuniformity of the oxygen distribution in the materials based on the Y123-phases can be due to the spinodal decomposition of the solution formed by the YBa₂Cu₃O₆ and YBa₂Cu₃O₇ phases.

An alternative model^{7, 8, 91, 92} relating the peak effect in the materials based on the R123-phases (R = Nd, Sm, Eu, Gd) to the fluctuations of the cation composition does not contradict the preceding model since it considers variations of the cation composition as a primary phenomenon responsible for a side effect, *viz.*, nonuniform distribution of oxygen. The possibility was reported^{7, 8, 92} of controlling the peak effect by different parameters of the process, such as the post-crystallisation annealing temperature, oxidation degree of the specimens and introduction of a 'cocktail' of REE dopants.

c. Methods of single-crystal growth

Unlike the production technology of polycrystalline materials, single-crystal growth is focused on growth of chemically and structurally homogeneous crystals of a specified size, shape, composition and controllable low level of defects and impurities. Meeting these requirements allows the crystals to be used in basic or applied investigations, e.g., in structural analysis,^{17, 235, 236} spectroscopy,^{237, 238} studies of oxygen diffusion,^{154, 157} atomic force microscopy,^{7, 8, 12} measurements of fundamental physical constants,¹⁹ etc.^{8, 239}

Anisotropy of the rate of crystal growth along crystallographic directions depends in a complex manner on the nature of REE and conditions of crystallisation.⁸ This can be due to the crystallographic anisotropy, different face energies and different mechanisms of the face growth. In turn, the growth anisotropy causes changes in the morphology and shape of the entire crystal. For instance, the crystals grown by spontaneous crystallisation are usually thin plates oriented perpendicular to the {001} direction,^{126, 240, 241} since the growth rate of the {100} faces is approximately five times higher than that of the {001} faces at high cooling rates (kinetic control). If the rate of melt cooling decreases down to 0.5–1.0 K h⁻¹, thick prisms-parallelepipeds or even isometric crystals are formed.²⁴¹ The {101}, {011} and {111} faces grow under these conditions along with the {100},

{010} and {001} faces, which indicates a quasi-equilibrium crystal growth (thermodynamic control).¹²⁶

The method of top-seeded crystal pulling from supercooled melt is characterised by a rather low supersaturation.^{8, 114, 239, 242} Such factors as the melt hydrodynamics and the distribution of temperature and concentration near the growing single crystal begin playing a significant role in this case (see S.13). By controlling the pulling rate and taking into account the growth anisotropy it is possible to obtain various 'bulk' single crystals, e.g., pyramidal crystals with expanded bases, large isometric crystals with a small angle of inclination of edges, pyramidal crystals with 'concave' bottom face and cylindrical crystals.^{8, 114, 239, 243} Other crystallisation methods allow the obtaining of needle-shaped and plate-like single crystals and crystals in the form of parallelepipeds as well.^{244–249} Thus, modern crystallisation methods make it possible to grow the HTSC crystals of any desired shape.

Crystallisation from melts is strongly affected by the nature of RE elements. In particular, introduction of 'light' REE can cause a chain of interrelated 'domino'-like changes in the characteristics of the R123-phases. The chain is as follows: an increase in the 'geometrical' stability → an increase in the thermal and thermodynamic stability → an increase in both the peritectic decomposition temperature and dissolution enthalpy of the R123-phases in melts → an increase in the solubility of REE and a decrease in the slope of the liquidus near the peritectic decomposition temperature, a decrease in the viscosity and acceleration of diffusion of the components in the melt. As a result, the crystallisation rate of the R123-phases containing 'light' REE (especially, Nd and Sm) should be higher than that of the same phases containing 'heavy' REE (Y, Yb, etc.) at a given supercooling degree of the melt, which favours the preparation of larger Nd123, Sm123, etc., crystals.¹¹⁴ The predicted regularities of the growth rate of 123-phases with different REE are observed experimentally, which can be seen from comparison of the growth rates along the direction of pulling the crystals grown by the modified Czochralski method:^{8, 114}

Phase	Y123	Y123	Pr123	Nd123
Atmosphere	air	oxygen	air	air
Growth rate /mm h ⁻¹	0.075–0.108	0.16	0.1	0.24

The growth rate of the crystals of a mixed (Y,R)123-phase was increased by doping the melt with samarium and neodymium.¹¹⁴

Unfortunately, the advantages of using 'light' REE to assist single-crystal growth and preparation of 'melt-processed' ceramics are combined with problems in controlling the chemical composition of products due to cation nonstoichiometry of the 123-phases containing 'light' RE elements. A simplified consideration of crystallisation in the frame of the Y₂BaCuO₅–Ba₃Cu₅O₈ quasibinary system is possible only for the 'point' Y123-phase (Fig. 25). In the case of systems whose phase diagrams contain regions where solid solutions can exist,⁸ the C° compositional point moves from the melt region L or a 422–L (PrBaO₃–L) two-phase region of the peritectic melt (at T = T_b), which contains particles of 'secondary phases' at elevated temperatures, to the R123ss–L two-phase region where the compositions of equilibrium solid [c(ss)] and liquid [c(L)] phases are determined at T_s < T_b (T_b > T_p) by tie-lines.

The ratio of the coefficients of cation diffusion in the melt plays a particularly important role in the establishment of an interrelation between the true compositions of the liquid and solid phases in the case of steady-state crystal growth. Obviously, the close values of these coefficients favour the choice of a tie-line that is the closest to the equilibrium tie-line. If the diffusion coefficient of a given cation is lower than those of other cations, the true tie-line is shifted with respect to the equilibrium tie-line.⁸ As a rule, the differences between the diffusion coefficients are not too large and the use of equilibrium phase diagrams makes it possible to correctly (quantitatively) predict the compositions of phases that crystallise under given conditions.

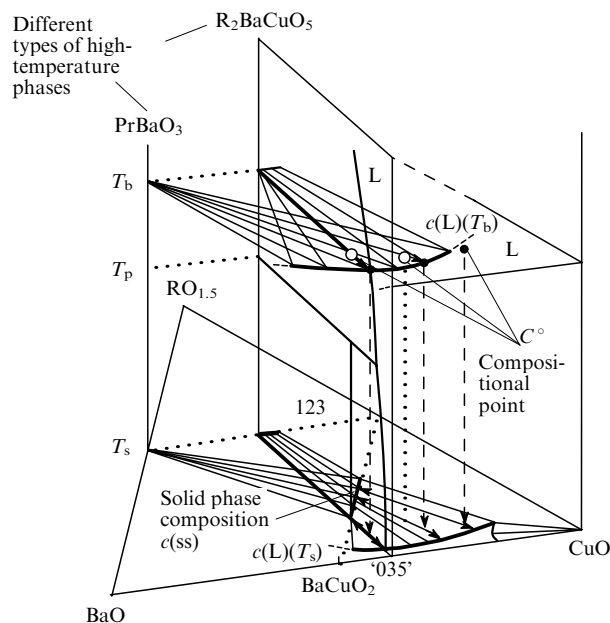


Figure 25. Supersolidus phase diagrams and single-crystal growth of HTSC.

Analysis of the data presented in Table 4 indicates that the volume of single crystals of the R123-phases can be appreciably increased and their perfection can be essentially improved²⁵⁰ using two modifications of the Czochralski method [the 'Solute-Rich-Liquid-Crystal-Pulling' (SRL-CP) and 'Top-Seeded-Solution-Growth' (TSSG) procedures].⁸ This is a universal method since it allows one to grow large single crystals of almost all R123-phases (R = Y, Nd, Sm, Pr) and (R₁R₂)Ba₂Cu₃O_z (R₁ = Y, R₂ = Sm, Nd) solid solutions^{8, 80, 81, 114, 251} as well as Nd_{1+x}Ba_{2-x}Cu₃O_z, Pr_{1+x}Ba_{2-x}Cu₃O_z, Nd_{1+x}Ba_{2-x}Cu_{3-y}.Ga_yO_z, YBa₂Cu_{3-y}Zn_yO_z phases, etc. According to the reported data,²⁵² superconducting crystals of the Pr123-phase can be obtained by the 'Top-Seeded-Floating-Zone' (TSFZ) procedure⁸ at reduced partial pressure of oxygen (see S.14).

Considerable attention has been paid recently on the development of growth methods of single-crystal high-temperature superconducting whiskers.^{76, 244, 253–256} The growth of whiskers in the systems with regions of solid solutions of the Bi–Sr–Ca–Cu–O^{254–256} and R–Ba–Cu–O (R = Sm,²⁴⁴ Nd⁷⁶) types was reported. It is known that this type of crystals possesses unique electrophysical²⁵³ and mechanical²⁵⁷ properties.

4. Preparation of long-length composites

Almost all the HTSC materials considered above (except for single crystals) are composites comprising the superconducting matrix and non-superconducting phases that determine specific properties and areas of application of a particular composite. For instance, highly disperse powders prepared by the chemical homogenisation methods are usually a mixture of different phases and dopants. The components of a film–substrate pair affect strongly each other. Large-grain ceramics are also a composite containing 'secondary phases' as inclusions in the superconducting matrix.

High-temperature superconducting silver-sheathed tapes are a typical example of industrial superconducting composites.^{16, 23, 54} To prevent thermoresistive instability of such tapes, they are fabricated as multifilament wires in which disappearance of superconductivity due to a local overheating above T_c will cause the current to flow round the resistive area through adjacent superconducting cores. Usually, superconducting wires are made of bismuth- or (more rarely) thallium-containing HTSC which possess higher plasticity and can be textured much easier than the

Table 4. The progress in the preparation of single crystals of the $\text{RBa}_2\text{Cu}_3\text{O}_z$ -phases.^{8, 114, 126, 239–256}

R	Single-crystal growth regime					Crystal size ^a mm × mm × mm	T _c /K	Note	Ref.
	flux	crucible	p _{O₂} /atm	cooling /°C	v _{cool} /°C h ^{−1}				
Spontaneous crystallisation (flux growth)									
Y	‘YBa ₄ Cu ₁₀ O _x ’	—	0.21	—	4–15	4 × 4 × 0.5	—	—	249
	~4 at.% Y,	Al ₂ O ₃	0.21	1010–960	0.5	5 × 5 × 2	88	—	126
	30 at.% Ba, 66 at.% Cu								
	Y : Ba : Cu = 1 : 6 : 18	Al ₂ O ₃ with polished walls	0.21	1000–970	0.1–0.4	5 × 4 × 1.5	90	temperature oscillations	251
	Y : Ba : Cu = 1 : 18 : 45	ZrO ₂ /Y ₂ O ₃	0.21	990–950	0.3–0.8	5 × 3 × 0.7	93.2	—	246
	64% Y ₁₂₃ –36%(7BaCuO ₂ + 11CuO)	Y ₂ O ₃	0.21	1050–970	0.5	4.3 × 4.3 × 3.6	91	temperature gradient	241
	0.13(1/6)YBa ₂ Cu ₃ O _y –0.87(0.28BaO + + 0.72CuO) + 1 mass % BaF ₂	Al ₂ O ₃	0.21	1000–900	2	20 × 10 × 0.5 12 × 10 × 1	93	—	119
	KCl : NaCl (1 : 1) + 5 mass % AgNO ₃	Al ₂ O ₃	0.21	1030–850	1	8 × 6 × 2	90	—	245
Y, Pr	1.5 mol.% Y ₁₂₃ , 2CuO · BaCuO ₂	ZrO ₂ /Y ₂ O ₃	5 · 10 ^{−3} →0.2	910	for 50 h	5 × 5 × 0.1	92	T = 910°C = const	220
	10 mol.% R ₁₂₃ , flux of an eutectic composition	BaZrO ₃ , density 98.5%	0.21	1005–950	0.7	2 × 2 × 0.5	91	—	248
	Nd	flux of an eutectic composition	ZrO ₂ /Y ₂ O ₃	0.05	1030–950	—	4 × 4 × 4	94.8	—
Floating zone melting									
La, Nd, Sm	Nd : Ba : Cu = 1 : 4 : 6–1 : 29 : 66	—	10 ^{−2} –10 ^{−4}	—	—	3 × 1.5 × 1.5 (single-crystal grains)	90 91 94	hot zone movement at 0.4–1 mm h ^{−1}	8
	Nd	Nd : Ba : Cu = 1 : 7.6 : 21.5	—	0.001	—	∅ 3 × 32	94	hot zone movement at 0.46–0.50 mm h ^{−1}	110
Top-seeded solution growth by crystal pulling (a modified Czochralski method)									
Y	0.15(1/6)YBa ₂ Cu ₃ O _y –0.85(0.3BaCuO ₂ – –0.7CuO)	Al ₂ O ₃	0.21	930	for 17 days	8 × 6 × 5	90	crucible rotation at 2–8 rpm	118
Y, Sm, Nd	211 + 0 : 3 : 5, 5 : 36 : 59	Y ₂ O ₃	0.21	1000	—	8 × 8 (5)	89	pulling rate 0.2 mm h ^{−1} , seed crystal rotation at 120 rpm	8
Y	211 + 0 : 3 : 5	Y ₂ O ₃ , ∅ 100 mm	0.21	1002–997	—	14 × 14 × 14 (angle of inclination of faces < 25°)	92	pulling rate 0–0.14 mm h ^{−1} , seed rotation at 120 rpm	8
	211 + 0 : 3 : 5, 5 : 36 : 59	Y ₂ O ₃	1.0	1015	—	19.8 × 19.5 (16.5)	92.7	pulling rate 0.05 mm h ^{−1} , seed rotation at 70–120 rpm, cooling in N ₂	114
Nd	(~0.84–1.98) at.% Nd, (28.49–28.16) at.% Ba, (70.67–69.86) at.% Cu	SnO ₂	0.21	1030–960	0.5	22 × 15 × 3	92	crucible rotation at 15 rpm, doping by Ga	251
	Nd : Ba : Cu = 0 : 0.78 : 1	Nd ₂ O ₃	0.21	1058–1070	for 67 h	24 × 24 (21)	95	pulling rate 0.1–0.25 mm h ^{−1} , seed rotation at 70–120 rpm	114

^a Values in parentheses refer to the height of the pyramidal crystal.

Table 5. Chemical compatibility of phases and the superconduction characteristics of the composites based on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ -phase doped with non-superconducting oxides.^{264–270}

Element (A)	Solubility/mol A/mol 2212			Phase in the 2212-matrix containing A			T_c /K (2212)	Pinning ^a
	in 2212	in a melt	T /°C	composition	size / μm	state		
Zr	<0.05	<0.05	1300	SrZrO_3	0.2	in 2212, agglomerated	93	0.092
Hf	<0.05	<0.05	1300	SrHfO_3	—	—	93	—
Sn	<0.03	<0.05	1300	$\text{Sr}_{1-x}\text{Ca}_x\text{SnO}_3$ ($x \approx 0.1$)	0.2	in 2212, agglomerated	90	0.074
Mg	<0.05	<0.1	1300	$\text{Mg}_{1-x}\text{Cu}_x\text{O}$ ($x \approx 0.1$)	1.0	in 2212	92	0.021
Al	<0.03	0.05	900	$\text{Sr}_{1.7}\text{Ca}_{1.3}\text{Al}_2\text{O}_6$	2–5	in 2212, agglomerated	90	0.026
Ga	0.15	0.8	900	$\text{BiSr}_{1.5}\text{Ca}_{0.5}\text{Al}_2\text{O}_z$	2–5	—	—	0.016
				$\text{Sr}_{1.3}\text{Ca}_{1.7}\text{Ga}_2\text{O}_6$	20	between 2212-grains	80	—
				$\text{Bi}_{0.2}\text{SrCa}_{0.8}\text{Ga}_2\text{O}_z$	10	—	—	—
				$\text{Bi}_{1.7}\text{Sr}_{2.3}\text{Ca}_{0.6}\text{Cu}_{1.6}\text{Ga}_{0.4}\text{O}_z$	—	—	—	—
In	<0.05	<0.1	900	$\text{Sr}_{1-x}\text{Ca}_x\text{In}_2\text{O}_4$ ($x \approx 0.55$)	0.5×5	in 2212, agglomerated	82	—

^a $\Delta M(60 \text{ K}, 10 \text{ mT})/\Delta M(5 \text{ K}, 1 \text{ T})$, where ΔM is the width of a hysteresis loop; this value for the undoped phase equals 0.01.

materials based on the R123-phases.^{258–263} Additionally, rather low melting temperatures of bismuth-containing HTSC provide a wider choice of metals and alloys for fabricating the sheath.

Silver is one of the most widely used materials for the outer sheath. It is plastic and relatively available, has high electrical and heat conductivity, causes no decrease in the transition temperature to the superconducting state of HTSC and serves as a specific membrane for oxygen exchange between the superconducting cores inside the tape and the gas atmosphere outside the tape. This system is closed as regards the mass transfer of bismuth, calcium, strontium and copper oxides. In addition, the walls of silver-sheathed tapes can favour nucleation and oriented grain growth near the surface areas of HTSC adjacent to the sheath,^{23, 54, 263} especially in the case of tapes with planar (ribbons) or pseudo-1D (multifilamentary wires) geometry. Often, the strength characteristics of the sheath are improved using the effect of dispersion hardening, *e.g.*, due to the formation of the MgO microcrystals in the silver matrix upon oxidation of silver–magnesium alloys by atmospheric oxygen.

The essential feature required of superconducting silver-sheathed tapes is that they be capable of carrying heavy currents. This first of all requires the attainment of perfect mutual orientation of highly anisotropic superconducting crystallites and exclusion of weak links between them. The negative effect of ‘secondary phases’ and gas evolution on peritectic melting or high-temperature annealing, which can cause a nonuniform current flow through the cross section of the tape, local violation of the optimum orientation of the HTSC grains and even shut off the orifice of the wire of size 1–30 μm , should also be prevented.

The optimum microstructure is usually formed by varying the composition, external gas atmosphere and thermal annealing regime. This requires a detailed knowledge of the phase diagrams.^{53, 54, 69, 263} To attain high transport characteristics of high-temperature superconducting tapes, it is also appropriate to use the methods of chemical homogenisation for preparation of highly disperse chemically and granulometrically homogeneous carbon-free powders for filling the silver sheathes that should undergo a plastic deformation. The methods used in the fabrication of superconducting silver-sheathed tapes should include (i) modern processes for the preparation of composites (‘powder-in-tube’, ‘tube-in-tube’, ‘rod-in-tube’ methods, *etc.*), (ii) thermomechanical treatment (repeated drawing and rolling) resulting in elongation of the silver sheath filled with powder by a factor of several tens, in an appreciable increase in the density of the superconducting cores inside the tape and in forced orientation of the HTSC grains along the deformation axis and (iii) low-temperature vacuum annealing to optimise the oxygen content inside the tape and to prevent bubbling.

Thus, it is now possible to fabricate tapes with a microstructure close to the desired one using modern processes and

production methods. However, the fundamental problem associated with a dramatic decrease in the critical currents of bismuth-containing HTSC (compared to other types of HTSC and first of all, to R123-phases) on raising the temperature or an increase in external magnetic field (see Fig. 4) remains unsolved. Therefore, the operating temperatures of bismuth-containing tapes are lowered to the liquid hydrogen temperature (20 K), despite the fact that their T_c values (90–110 K) are higher than the boiling point of a cheap coolant, liquid nitrogen (77 K), which is effectively used with other types of HTSC.

The most promising way of increasing the critical current density for bismuth-containing high-temperature superconducting materials is associated with the preparation of composites with uniformly distributed microscopic inclusions of non-superconducting phases formed by the constituents of the system or by introducing ‘alien’ phases compatible with the HTSC.^{264–270} The main characteristics of the composites thus prepared (homologues of the 2212- and 2223-bismuth-containing HTSC) are presented in Table 5. As can be seen, the most pronounced positive effect is observed with zirconates and stannates, although there are many phases compatible with the high-temperature superconducting matrix which do not result in appreciable decrease in its T_c and do not suppress the HTSC formation dynamics. At the same time, measurements of physical properties indicate an increased stability of superconducting characteristics of the composites.²⁷⁰ Obviously, this promising investigation line will be developed in the future.

V. Practical applications of high-temperature superconducting materials

The possibility of practical applications of high-temperature superconducting materials has opened fresh opportunities for microelectronics, medicine, production of efficient energy storage and power transmission systems and industry as a whole.^{7, 8, 15, 16}

The use of high-temperature superconducting films allowed production of small-scale systems belonging to a new generation of communication devices including electromagnetic screens, modulators, antennas, commutators, filters of microwave and pulse signals, multilayered film hetero-structures including dielectric, ferroelectric and normal metal layers in addition to the HTSC layers. Such films made it possible to develop bolometers operating in the millimetre, submillimetre and infrared bands, basic circuit arrangements of superfast computers, ultrasensitive tomographs and diagnostic devices capable of responding even to changes in the mental condition of a man (measuring devices based on the Josephson effect).

High-temperature superconducting tapes with high superconducting characteristics can actually be used in practice for

production of super-power magnets and lines for nondissipative transmission of electrical power. Currently, silver-sheathed tapes can be manufactured commercially. Large-scale production and wide use of these tapes are still limited by high cost. Nevertheless, many small-scale systems and test lines are already at work.

The prospects of using HTSC based on the 123-phase are associated with the possibility of production of bulky items of a rather simple shape using the most suitable and operationally convenient methods. Such items can be divided into two classes. The first of them comprises the specimens characterised by a high ability to shield the external magnetic field or to be repelled by the field. This ability can be characterised by the so-called levitation force, which is dependent on the intracrystallite critical current density. The other class comprises the specimens of high-temperature superconducting materials with high transport (intercrystallite) current. In the future, such ceramic devices can find practical use in the production of permanent magnets with 'frozen-in' magnetic flux, magnetic repulsion trains (the MAGLEV project), flying wheels, bearings rotating virtually without friction, efficient and economical motors, super-power generators and transformers, magnetic separators, superconducting relays, fast current limiters, powerful nondissipative electrical current leads, medical tomographs, powerful magnetic systems for thermonuclear fusion and accelerators of elementary particles (new-generation Tocamac) and, finally, magnetohydrodynamic generators.

Preparation of substrates in thin film technology and micro-electronics seems to be the most realistic practical use of large single crystals of HTSC. Such substrates should be characterised by small mismatch between the unit cell parameters and those of materials of the films, have close TEC values and favour epitaxial growth of films. Additionally, all crystallochemical and thermomechanical parameters of high-temperature superconducting single-crystal substrates can be precisely adjusted by using solid solutions with different types of substitution of the yttrium and barium positions.

Supplement

S.1. The presence of a metastable orthorhombic BaCu_3O_4 phase [$a = 10.986(3)$, $b = 5.503(1)$, $c = 3.923(1)$ Å] was found in thin films of the R123-phase.²⁷¹ Stabilisation of this phase requires the formation of a coherent interface between the phase and surrounding high-temperature superconducting matrix. The BaCu_3O_4 phase decomposes if the film thickness exceeds ~ 0.3 μm .

S.2. Discrepancies in determination of the limits of oxygen nonstoichiometry in BaCuO_{2+z} can be due to the formation of oxycarbonates [e.g., $\text{Ba}_{44}\text{Cu}_{48}(\text{CO}_3)_6\text{O}_{87.9}$, see Aranda and Attfield²⁷²] or to an ambiguous assignment of the specimens with other cation compositions to this phase.^{273, 274} A reliable thermodynamic assessment of the Ba–Cu–O system was reported.²⁷³ The oxygen nonstoichiometry in the Ba_2CuO_3 -, BaCuO_2 - and $\text{Ba}_2\text{Cu}_3\text{O}_5$ -phases was also discussed.^{274–276}

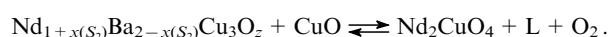
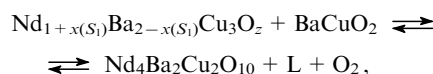
S.3. The low-temperature decomposition of $\text{NdBa}_2\text{Cu}_3\text{O}_z$ was considered.²⁷⁷ It was established that degradation of superconducting properties of high-quality polycrystalline specimens ($T_c = 94$ K) in the temperature range 450–750 °C occurs nonlinearly depending on the 'ageing' temperature and duration of low-temperature isothermal annealing. Prolonged annealing at 400–600 °C for 450 h in air can result only in a slight decrease in T_c after complete oxidation of the sample ($T_c = 89$ K), whereas the annealing at 700 °C for 165 h brings about a decrease in T_c by 11 K.

S.4. The first reliable determination of the structure of a low-temperature (oxidised) modification of the $\text{Nd}_{1.9}\text{Ba}_{1.1}\text{Cu}_3\text{O}_z$ -phase using the data of X-ray, electron and neutron diffraction experiments and IR and Raman spectroscopy was reported recently.²⁷⁸

Studies carried out by neutron diffraction, differential scanning calorimetry, Raman and Mössbauer spectroscopy and EXAFS have confirmed that, unlike the $\text{NdBa}_2\text{Cu}_3\text{O}_z$ -phase, oxidation of the $\text{Nd}_{1.9}\text{Ba}_{1.1}\text{Cu}_3\text{O}_z$ -phase can occur owing to 'one-dimensional' oxygen diffusion along the b axis of the structure. This is accompanied by a second order phase transition resulting in the appearance of an inversion centre (the high-temperature modification has the $Amm2$ space group vs. the $Ammm$ group for the low-temperature modification²⁷⁸), ordering of the oxygen sublattice and coupled zigzag-shaped displacements of copper atoms from the 'ideal' positions at the centres of perovskite-like structural blocks, which is most likely due to 'compression' of the structure along the long axis c caused by introduction of extra oxygen atoms.²⁷⁹

S.5. Discussion of the charge transfer between the superconducting planes and dielectric block using the results obtained by X-ray structural analysis and Raman spectroscopy can also be found elsewhere.^{278, 280}

S.6. At a given partial pressure of oxygen, the compositions with the minimum $x(S_1)$ and maximum $x(S_2)$ substitution degrees in the $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ solid solution are fixed, because they correspond to the invariant quinary equilibria (the number of degrees of freedom is $4 - 5 + 2 - 1 = 0$)



The corresponding phase transformation temperatures are also fixed, which provides the optimum conditions for achieving the above-mentioned substitution degrees. For instance, it was experimentally established that a temperature range between 985 and 1030 °C is optimum for preparation of the $\text{NdBa}_2\text{Cu}_3\text{O}_z$ phase with $T_c \simeq 94$ K (at $p_{\text{O}_2} = 0.21$ atm).²⁸¹

S.7. One of the most promising and intensively developing universal approaches to computer simulation of crystallisation of HTSC systems is the phase field concept for multiphase systems (PFCMS).²⁸² In the classical nucleation models, the liquid–solid interface is assumed to be infinitely thin. The PFCMS model considers a liquid–solid interface of finite thickness. Obviously, this is a great stride toward deriving a fundamental generalisation of crystallisation mechanisms. An additional continuous function (the phase field) is also introduced in this model, which plays the role of the order parameter used for identification of the regions of the liquid and solid states. In the simplest case (one solid phase in melt), the phase field can be described using a function $p(x, t)$ whose values vary between 0 and 1. If $p(x, t) = 1$, then at a point x and at instant t the system is in the solid state, whereas $p(x, t) = 0$ corresponds to the liquid. The liquid–solid interface is described by all $p(x, t)$ values between 0 and 1. The following equation for the phase field function was derived²⁸² by minimising the density of the free energy of the system

$$\tau[\dot{p}(x, t)] = \varepsilon \nabla^2 p(x, t) - f'(p) + m(p, T, c).$$

This equation includes most of the physically important melt solidification parameters such as the (free) energy gradient ε ; the crystallisation front propagation velocity (by means of the orientation-dependent function τ , which describes an anisotropic or facet growth); the derivative $f'(p)$ of the potential determining the phase boundary stability under equilibrium conditions, as well as the driving force $m(p, T, c)$ of the process, which is proportional to the degree of deviation from thermodynamic equilibrium and should include the temperature dependence $T(x, t)$ and the concentration profile of the distribution of constituents (c). The necessity of inclusion of the function c is explained by considering the diffusion processes occurring in the system (e.g., the dissolution rate of the solid phases in the melt).

S.8. The mechanism of the needle-shaped crystal growth under isothermal conditions remains unclear as yet. At the same time, this phenomenon is not observed for those REE of the yttrium subgroup whose R123-phases do not form the barium ← REE substitution solid solutions. It was also established²⁸¹ that the reason for growth of the needle-shaped crystals is closely related to the features of the phase diagram of the Nd–Ba–Cu–O system, in particular, to the increased deviation of the composition of the equilibrium phase of the $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ solid solution towards $x > 0$ which occurs on raising the temperature. In this case, the phase with $x = 0$ decomposes on heating with the formation of a solid solution with $x \approx 0.1$, a non-superconducting $\text{Nd}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$ phase and a melt L. At the initial moment, the composition of the liquid phase L can differ from the equilibrium composition, thus providing the driving force for the growth of $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_z$ and $\text{Nd}_4\text{Ba}_2\text{Cu}_2\text{O}_{10}$ crystals not only under isothermal conditions, but (probably) also even with increasing temperature (mention may be made here that single crystals of HTSC are usually obtained by cooling of melts).

S.9. Single-phase specimens of mercury-containing HTSC and especially mercury-containing crystals can hardly be obtained because of extremely high volatility of mercury and its compounds. Therefore, the preparation of the crystals of the most promising Hg1223-homologue with unique physical characteristics²⁸³ by the ampoule synthesis is of considerable interest. Single crystals of $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_z$ ($n < 4$) with $T_c \approx 130$ K were synthesised by spontaneous crystallisation from PbO or BaCuO_2 –CuO flux in a crucible made of stabilised zirconium dioxide (crystallisation temperature $930 < T < 1070$ °C) in an autoclave at an Ar pressure of $(10–15) \times 10^3$ atm.^{284, 285} Introduction of rhenium in order to stabilise the structure makes it also possible to grow single crystals of $\text{Hg}_{0.75}\text{Re}_{0.22}\text{Ba}_2\text{Ca}_5\text{Cu}_6\text{O}_{15}$ ($T_c = 100$ K) and $\text{Hg}_{1-x}\text{Re}_x\text{Ba}_2\text{Ca}_6\text{Cu}_7\text{O}_{16+4x+z}$ ($T_c = 84$ K) homologues.⁶⁸

S.10. The uniqueness of the HTSC–manganite hetero-structure²⁸⁶ shown in Fig. 21 is that it comprises two promising and intensively studied phases with nonlinear electrophysical properties, viz., the superconducting cuprate phase and the manganite phase exhibiting a giant magnetoresistance effect. Such hetero-structures are promising for the use in microelectronics.

A microstrip resonator can be considered as an example of devices manufactured using conventional elements (HTSC-films and a dielectric substrate). In this case, the double-sided deposition of a superconducting film on the single-crystal substrate was carried out by CVD methods.²⁸⁷

S.11. Phases of the $\text{RBa}_2\text{Cu}_3\text{O}_z$ type can be synthesised over a period of about 10 to 30 min at 500–550 °C using a mechanoactivated decomposite mixture, i.e., a mixture of copper-free and copper-rich reagents ($\text{Y}_4\text{Ba}_3\text{O}_9$ and CuO) compacted at 250 °C.²⁸⁸

S.12. Recently, the formation of antisite defects in the barium and neodymium sublattices in the fully oxidised $\text{NdBa}_2\text{Cu}_3\text{O}_{6.9}$ phase with a low transition temperature to the superconducting state was found by X-ray spectral and X-ray structural analysis and by Raman spectroscopy.²⁷⁹

S.13. A cuprate melt considered as a high-temperature solvent is characterised by a density from 4.8 to 5.4 g cm^{−3}. The minimum density is observed for an eutectic composition 28 mol. % BaO:72 mol. % CuO.²⁸⁹ Such melts have similar temperature dependences of the surface tension and viscosities which increase as the BaO concentration increases.²⁸⁹ Above 955 °C, the surface tension coefficient of the melt lies in the range $\sim 0.3–0.6$ N m^{−1}. The calculated radii of the viscous flow units suggest that the melts have a ‘slightly ionic’ nature and a low aggregation degree of the ions in the melt. The melts exhibit a mixed (mostly electron-type) conductivity.

Two factors should be considered when discussing the limiting stages of single-crystal growth from a liquid (in particular, by the modified Czochralski method). First, this is the steady-state

growth of the single crystal. This requires meeting the condition for the balance of the amount of R_2O_3 in the flux and that necessary for the deposition of the R123-phase on a crystal face, written over the liquid–solid interface. Second, crystallisation can be characterised by relatively high near-boundary supersaturation with respect to R_2O_3 (in the so-called boundary layer) due to kinetically hindered crystal face growth. The following approximate formula for the crystal face growth rate (v), which includes the diffusion of Y^{3+} ions in the melt, was proposed⁸ under some assumptions as a first approximation.

$$v = \frac{D_L^{2/3} \omega^{1/2} [(T_b - T_p)/m_L^{211} + (T_p - T_i)/m_L^{123}]}{1.6v^{1/6}(c_s^{123} - c_i)}$$

Here, D_L is the coefficient of bulk diffusion from the Y_2O_3 source phase (Y_2BaCuO_5) contacting the melt at the temperature T_b to the face of the $\text{YBa}_2\text{Cu}_3\text{O}_z$ crystal (the peritectic decomposition temperature T_p) that grows from the melt at the temperature T_i ; ω is the angular velocity of crystal rotation; m_L^{211} and m_L^{123} are the slopes of the tangent to the liquidus above and below T_p ; v is the kinematic viscosity of the melt; and c_s^{123} and c_i are the concentrations of Y^{3+} ions in the solid phase (crystal) and in the melt near the growing crystal, respectively. The maximum crystal face growth rate that can be achieved in the absence of kinetic complications is $v_{\max} \approx 0.36$ mm h^{−1}. However, it is 3 times higher than that observed experimentally (0.108 mm h^{−1}). This indicates that the growth of single crystals of the Y123-phase using the modified Czochralski method is likely to be controlled not only by diffusion of the components through the melt, but also by the interphase kinetics of deposition of the Y123-phase.

The hydrodynamic conditions of the experiments on the growth of large HTSC-crystals and their effects on the morphological features of $\text{RBa}_2\text{Cu}_3\text{O}_z$ crystals have been analysed in detail using the generalised ‘dimensionless analysis’ approach.²⁹⁰ Growth of a crystal by the modified Czochralski method is characterised by an increase in the diameter of the crystal with time, which continuously changes the conditions for crystal growth. Generally, the relative contribution of convection due to (i) the density difference between the melts with different temperatures (natural convection) and (ii) rotation of the crystal (forced convection) can be assessed as the ratio of the Reynolds and Grashof numbers. The dimensionless temperature

$$\Theta = \frac{T_i - T_{\text{top}}}{T_b - T_{\text{top}}}$$

of the ‘crystal–melt’ contact surface (T_i) and the top region of the crucible (T_{top}), normalised to the overall temperature gradient between the bottom (T_b) and top regions of the crucible can be estimated (from experimental data) as $\Theta = 0.47\text{Re}^{0.028}\text{Pr}^{0.041}\text{Gr}^{0.019}\text{Dsc}^{0.064} + 0.10$ (Dsc is the geometrical factor). According to this expression, the steady-state crystal growth requires a precise control over the rotation velocity taking into account the increase in the crystal diameter during the growth. Otherwise, a crucible of a large diameter should be used.

S.14. The results of recent studies confirm the existence of a superconducting $\text{PrBa}_2\text{Cu}_3\text{O}_7$ phase; however, this issue remains a moot question as yet.^{291, 292}

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Methods for preparation of carbon nanotubes

E G Rakov

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Abstract. The most important methods of synthesis and purification of carbon nanotubes, a new form of material, are described. The prospects for increasing the scale of preparation processes and for more extensive application of nanotubes are evaluated. The bibliography includes 282 references.

I. Introduction

Immediately after they had been discovered in 1991,¹ carbon nanotubes (nanotubulenes, hereinafter, NT) attracted so much attention of scientists of various professions that the discoverer, Iijima, soon became and still remains one of the most cited researchers in the field of nano-sized materials. The reason for this interest is not the unusual structure of these compounds, as in the case of fullerenes (although this also plays a certain role) but rather the prospects that are opened by the properties of NT for materials science.

The journal *Fullerene Science and Technology*, having the word 'technology' in its title, was founded in 1992; during the decade which has passed since the discovery of fullerenes (by 1995), 150 patents for their use were granted in the USA;² reviews dealing with commercialisation of the manufacture and use of fullerenes appeared;³ however, there are still no data on the large-scale implementation of any patented method or, even more so, on the appearance of a new line of research in the materials science.

The situation with NT is absolutely different: as early as 1992–1993, the main fields of their potential application took shape and design of the first prototypes of future devices started. Some applications of NT were inherited from fullerenes (electrodes for chemical cells, safe sources of hydrogen in transport devices, optical filters), other applications coincide with those of carbon fibres (high-strength composites), and some fields of application are due to the unique properties of NT themselves (semiconductor devices, field emitters, probes of tunnelling microscopes, 'quantum wires'). It is clear that this is by no means the full

list of currently known applications of NT. It is not without reason that a recent review⁴ is entitled 'Nanotubes: a revolution in materials science and electronics'. As Buchachenko has noted vividly, carbon nanotubes made it possible 'to pass from fine words to impressive deeds'.⁵

Certainly, fullerenes, too, are finding and will be finding application (the rapidly progressing chemistry of fullerenes is now at an early stage of development); however, NT as materials have already clearly separated from their three-dimensional relatives.

Defect-free carbon NT are formed as a result of rolling of planar atomic network graphite sheets (graphenes) into seamless cylinders with diameters of ~1 to 120–150 nm and with lengths of up to hundreds micrometers. There exist three forms of NT: achiral NT of the 'armchair' type (two sides of each hexagon are oriented perpendicular to the NT axis), achiral 'zigzag' NT (two sides of each hexagon are parallel to the NT axis) and chiral or helical NT (each pair of the hexagon sides is arranged at an angle other than 0 or 90° relative to the NT axis).

The structures of NT are usually described by means of two indices, n and m , which are related unambiguously to the NT diameter (d) and the chiral angle (θ , characterising the deviation from the 'zigzag' configuration and ranging from 0 to 30°) (Fig. 1).

$$d = \frac{a\sqrt{3(n^2 + m^2 + mn)}}{\pi},$$

where a are the interatomic distances in the planar network,

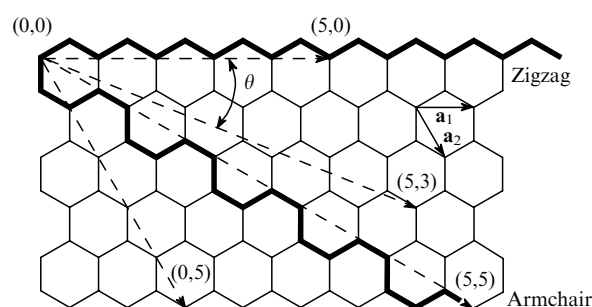


Figure 1. Scheme illustrating the structure of idealised NT.

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$$\theta = \arctan\left(-\frac{\sqrt{3m}}{2n+m}\right).$$

Thus achiral NT of the ‘armchair’ type are characterised by indices (n, n) , those of the ‘zigzag’ type have indices $(n, 0)$ and chiral ones are described by (n, m) .

Nanotubes can be single- or multi-walled; the number of walls is theoretically unlimited but normally it does not exceed a few dozen. The distances between the neighbouring shells are close to the interlayer spacing in graphite (0.34 nm); thus, the smallest diameter of carbon NT is ~ 0.7 nm. The diameter of the second and subsequent coaxial atomic layers is stipulated by the diameter of the innermost layer. In this connection, the structure of NT resembles that of onion fullerenes; if the inner shell is C_{60} , the second shell is C_{240} , the third one is C_{540} , etc. The spatial accordance of the structures of NT layers, *i.e.* retention of interatomic distances close to 0.34 nm is possible only provided that the chiral angle changes on passing from layer to layer.

The specific structural features of NT can hamper their use as materials — synthesis gives NT with different structures. Multi-walled NT are much more diversified; therefore, more uniform single-walled NT, which, in addition, usually contain fewer defects, are preferred for the design of functional materials.

In most cases, the tips of NT are covered by hemispherical or conical caps, which contain not only hexagons but also pentagons, in which the configuration of the carbon atoms is less stable. These caps are somewhat more chemically reactive than the lateral surfaces. The hemispherical caps resemble ‘halves’ of fullerene molecules. Thus the NT (10,10), isolated rather frequently, are capped by halves of spherical C_{240} fullerene.

Synthesis of NT can give a tough precipitate consisting of sintered NT, a somewhat softer precipitate of densely stacked NT, a rubbery material consisting of entangled NT (‘paper’, ‘mats’), a three-dimensional network of long fibres (‘lace collar’, ‘web’), or a textured material consisting of parallel or nearly parallel (but arranged at a distance from one another) NT on a substrate (‘forest’). Structures looking like a ‘sea-urchin’ and NT as helices (see below) have also been described.

Nanotubes tend to form relatively stable aggregates (they are referred to as bundles or ‘ropes’), in which the axes of individual NT are parallel to one another, the shortest distance between them being ~ 0.32 nm (Fig. 2). These aggregates arise due to van der Waals forces.

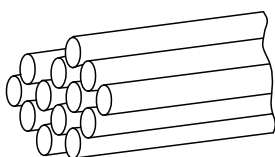


Figure 2. Schematic structure of bundles of single-walled NT.

In the majority of cases, the synthesis of carbon NT is accompanied by the formation of other carbon modifications — fullerenes, nanoparticles and amorphous carbon. The yields of NT and side products are determined by the conditions of synthesis; the removal of side products is an important stage in the synthesis of NT.

Good prospects for the design of new functional and structural materials are opened by modification of carbon NT, which can be accomplished by the following methods:

- (1) filling of the inner cavities of NT with substances which alter their electronic, magnetic or mechanical properties;
- (2) ‘grafting’ of functional groups to the tips of NT;
- (3) replacement of some of the carbon atoms in NT by atoms of other elements;
- (4) partial or complete cleavage of double bonds on the lateral surfaces of NT by adding one or another reagent;

(5) intercalation (insertion) of ‘guest’ atoms or molecules into the intertubular space of NT bundles.

In addition, NT can be used as templates in the template syntheses of nanotubular or nano-rod materials for various purposes.

The scope of this review is restricted to the methods of synthesis of NT because these methods are important for the development of studies and projects related to NT. They should lay the grounds for the future commercial manufacture. Attention is focussed on recent studies.

The publication in 1999 of a Russian review devoted to the structure, electronic properties and morphology of NT⁶ facilitated the performance of this task. Earlier Russian reviews dealing with the mechanisms of the formation of fullerenes, nanoparticles and NT^{7,8} were also useful; however, they are somewhat less significant because lots of newer studies have appeared.

Apart from carbon NT, those containing B and N atoms are also briefly considered in this review. These NT can be synthesised either from carbon NT or simultaneously with them.

II. Electric-arc synthesis

It is known that an electric arc develops a temperature of up to 4000 °C, its ‘burning’ being accompanied by transfer of a substance between the electrodes. In 1990, electric arc-synthesis with graphite electrodes under an atmosphere of inert gases was first used to prepare fullerenes in relatively large amounts.⁹ It is among the products of arc synthesis that Iijima discovered carbon NT in 1991.¹ Subsequently, this procedure has been modified and used in many laboratories of different countries.

1. Principles of the method

The first synthesis of NT in relatively large (gram) amounts was also performed in Japan.¹⁰ The electric-arc synthesis was carried out under a helium atmosphere using graphite electrodes — an anode 8 mm in diameter and a cathode 12 mm in diameter — located at a distance of less than 1 mm from each other. The current in the arc reached 100 A (current density ~ 150 A cm⁻²) and the voltage was 10 to 35 V. The rate of the growth of the cathode deposit was ~ 1 mm min⁻¹. Some of the graphite evaporated from the anode turned into carbon black and soot, which were deposited on the walls of the reaction chamber, and some was deposited at the cathode. The outer solid layer of the cathode deposit contained sintered NT and nanoparticles, which could not be separated. The purity and yield of NT depended appreciably on the helium pressure — the formation of NT started at ~ 13 kPa, and at 66–332 kPa, the cathode deposit contained only NT and nanoparticles. The optimum pressure was 67 kPa; in this case, $\sim 75\%$ of the electrode material consumed was deposited at the cathode, the yield of NT, which were accumulated in the inner, black, relatively soft part of the deposit being $\sim 25\%$.

The yield of NT attained in an argon flow was much lower than that in a helium flow.

Analysis of the results of the first studies on the structure and synthesis of NT^{10–14} allowed Ebbesen^{15, 16} to note some characteristic features. The material formed has a hierarchical structure, in which tens or hundreds of individual multi-walled NT with diameters of 2–20 nm and nearly equal lengths (microns or tens of microns) are joined into regularly organised bundles resembling ropes. These ropes are combined into fibres with a diameter of ~ 50 μ m, while the fibres are joined into threads having even greater diameters (about a millimeter) and visible with the naked eye. The larger the bundle, the more disordered can it be.

The formation of columns ~ 50 μ m in diameter consisting of NT and arranged parallel to the electrode axis has been reported.¹⁷ This study is notable due to the setup used; it had movable vertical electrodes with a diameter of 19 mm, which (as well as the arc area) could be cooled during the process. (In the conventional arc syntheses, the cathode and anode diameters are different, the anode diameter being smaller than the cathode

diameter.) Using this setup controlled by a computer, the researchers were able to deposit $\sim 90\%$ of the substance at the cathode and to obtain thus high-quality multi-walled NT. The current in the arc of this setup reached 250–300 A, although the current density at the beginning of the process was even lower than the standard value and amounted to $70\text{--}80\text{ A cm}^{-2}$. Upon annealing in air at $650\text{ }^{\circ}\text{C}$, the columns were etched being replaced by channels surrounded by entangled NT.

An increase in the electrode diameter normally causes sintering and cracking of NT. A dense greyish product is accumulated in the inner part of the cathode deposit, instead of the easily extractable black material. This phenomenon was initially explained by insufficiently high temperature of the synthesis;¹⁸ however, the assumption that the temperature was, conversely, too high seems more reasonable.¹⁷

The decrease in the anode diameter from 12.7 to 8.0 mm with the cathode diameter (25.4 mm) and current density (140 A cm^{-2}) remaining the same increased the yield of NT. An increase in the pressure of helium (which is believed to quench NT) from 6.6 to 101 kPa also resulted in an almost proportional increase in the rate of growth of the deposit.¹⁸ However, according to Ando and Iijima,¹⁹ variation of the yield of NT as a function of gas pressure passes through a maximum, the position of which corresponds to 7 kPa in the case of Ar or CH_4 and to 3 kPa for He. In the opinion of Wang *et al.*,¹⁸ the discharge used in the synthesis of NT is quasi-continuous and has a characteristic interruption frequency of $\sim 8\text{ Hz}$. The discharge is initiated between the closest sections of the electrodes and, after some amount of graphite has been evaporated from the anode (which extends the discharge), it ‘jumps’ to the neighbouring section and thus becomes shorter. Travelling of the arc over the electrode surface changes presumably the sites of localisation of NT.

Lozovik *et al.*⁷ believe that an arc discharge between graphite electrodes has two modes of operation, a noisy and a quiet one, transition from one mode to the other being induced by changes in the current density. A high current density and a low inert gas pressure (noisy mode) result in the predominant formation of fullerenes, while nanoparticles and NT are formed predominantly at a relatively low current density and a high pressure (quiet mode).

A thorough investigation of the cross-sections of bundles obtained by the arc method showed that NT do not have, as a rule, a cylindrical shape.²⁰ The cross-sections of NT look like polyhedra or ellipses with numerous defects including edge dislocations. The structures of NT are intermediate between the ‘Russian doll’ model (coaxial seamless cylinders) and the ‘folded carpet’ (‘scroll’) model. In earlier studies, either model has been preferred, although the methods used in the investigations did not allow one to reveal the differences between them.²¹ Moreover, it was found that the ‘scroll’ model is too regular to describe many NT and, in some cases, the ‘papier-mache’ model (separate fragments applied onto one another) should be accepted (Fig. 3).²²

Some disordering of the structure is due to the fact that NT are formed in the arc under non-equilibrium conditions and to the stress arising upon joining of individual NT into bundles. The presence of a large number of defects in multi-walled NT obtained in an electric arc is confirmed by experiments on their intercalation.^{23, 24}

It has been suggested²⁵ that bundles are formed under the influence of an electric field, their length, diameter and the manner of laying being dependent on the electric field strength. However, in reality, bundles can be formed even without electric fields. Nevertheless, it is beyond doubt that the field has an influence on the morphology of the products of arc synthesis.

The yield and shape of NT formed in an arc discharge plasma depend not only on the main arc discharge variables (the voltage between the electrodes, the current strength and density, temperature of the plasma) and parameters related to the discharge

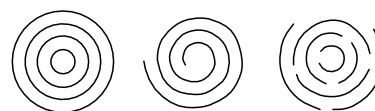


Figure 3. Structure models of multi-walled NT. (a) ‘russian doll’; (b) ‘scroll’; (c) ‘papier-mache’.

variables (the pressure and composition of the inert or reacting gas) but also on the gas flow rate, on the dimensions of the reaction chamber, and on the duration and the scale of the process. The configuration of cooling devices if they are present (determines the size and shape of temperature fields) and the power of cooling devices (determines the heat removal), the nature and purity of the electrode materials and several other parameters that can hardly be quantitatively evaluated are also significant.^{10, 15–19, 26} The main parameters governing the yield of NT — the rates of NT growth and quenching — depend on numerous variables which are far from being fully taken into account in experimental studies. This accounts for some contradictions, hampers comparison of the results and often makes them poorly reproducible. The absence of theoretical models (related to the setup geometry), which makes scaling impossible, might be due to the same reasons.

The mechanism of the formation of NT in an arc discharge has not yet been unambiguously elucidated, although it is discussed in many studies. There exist two main opposing models. According to one model, growth of NT advances due to the addition of carbon atoms or fragments from the vapour phase to the dangling bonds at the tips of open NT, whereas according to the other model, they add to the topological defects in the caps of closed NT. In recent years, preference is given to the former model, because the occurrence of ‘edge-to-edge’ (‘lip–lip’) interactions has been proved. They prevent the formation of caps in multi-walled NT due to the formation of ‘fluctuating’ (closure–rupture) C–C bonds at the tips of two or three neighbouring coaxial NT.^{27, 28}

The role of the electric field in the mechanism of the formation of NT is obviously overstated in some publications. It has been shown^{16, 29} that this role is far from being paramount, the NT growth involving simultaneously charged (C^+ *etc.*) and neutral (C_2 *etc.*) carbon species. The difference between the main carbon sources might account for the formation of two types of condensed products, NT and polyhedral particles. It is also unlikely that the tips of NT growing at the cathode in an arc discharge are opened due to strong electric fields.³⁰

The experimental studies considered above describe the preparation of multi-walled NT. The formation of single-walled NT was first observed by Ajayan and Iijima,³¹ but this study has not been adequately appreciated, later studies being regarded as the pioneering ones.^{32, 33} Both groups of researchers cited^{32, 33} performed the synthesis in the presence of catalytic additives. This opened up a new chapter in the history of NT.

2. The influence of catalytic additives

The pioneering studies^{32, 33} somewhat contradict each other in details but coincide in the main point stating that the introduction of small amounts (1%–2%) of transition metals such as Fe, Co, Ni or their mixtures into the graphite anode influences appreciably the shape and the yield of NT and, in some cases, also localisation of the NT-containing product in the reaction chamber.

Subsequently, admixtures of Li, Cu, Ag, Zn, Cd, B, Al, In, Y, La, lanthanides, Si, Ge, Sn, Ti, Hf, Pb, Sb, Bi, S, Se, Cr, W, Mn, Ru, Pd, Pt, mixtures of two metals or of a metal with a nonmetal and several carbides and oxides were tested.^{28, 34–37} It was found that vaporisation of an anode containing Co, Co–Ni, Co–Y, Co–Fe, Ni, Ni–Y, Ni–Lu and Ni–Fe gives deposits looking

like a lace collar or a soft belt being formed around the cathode deposit. They contain single-walled NT mixed with amorphous carbon and metal particles, the NT having diameters of 1.2–1.4 nm and being joined into more or less ordered bundles. The tips of single-walled NT are closed and contain no metal particles. Upon evaporation of graphite anodes with Ni–Y and Co–Y admixtures, the content of single-walled NT in the deposits reaches 70%–90%.³⁷ The yield of NT also markedly increases when a Co–Pt mixture is used.³⁸

Some catalysts (Cu; Cu with Ni, Pt, Y or Fe; Ni; Ni with Y, Lu or Fe) caused the formation of a ‘web’, which hung between the cathode and the walls of the chamber. This web, as well as the deposit on the chamber walls, contained fullerenes, amorphous carbon, flat graphite particles and small amounts of single-walled NT. In some cases, a rubber-like deposit was formed on the walls; it could be detached as pieces or ribbons (Fig. 4).³⁹

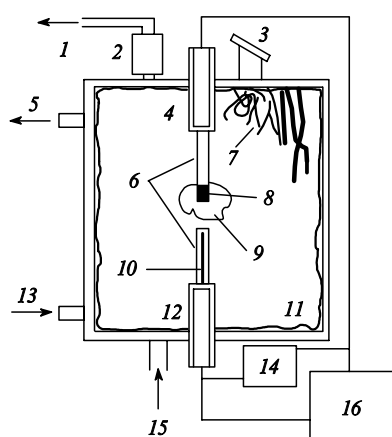


Figure 4. Setup for electric arc synthesis and localisation of various products;

(1) to vacuum pump; (2) filter; (3) viewing window; (4) cathode; (5) nozzle for the removal of the cooling water; (6) graphite electrodes; (7) web-like precipitate; (8) cathode deposit; (9) rubber-like deposit around the cathode; (10) filling material (a mixture of powdered graphite with a metal); (11) fullerene- and NT-containing soot on the walls; (12) anode; (13) nozzle for the supply of cooling water; (14) voltmeter; (15) helium inlet; (16) power supply.

The addition of sulfur to a Co catalyst also resulted in a greater amount of the web-like product and higher NT yields and in a quite noticeable scatter in the NT diameters (from 1 to 6 nm).⁴⁰ Evaporation of Co and S simultaneously with graphite changed the shapes of the resulting products and led to the evolution of multi-walled NT in the middle of the cathode deposit, multi- and single-walled NT together with many other particles in the rubber-like deposit around the cathode, and single-walled NT in the web-like material.³⁹

Kiang *et al.*⁴⁰ believe that the multi- and single-walled NT are formed *via* different mechanisms and that Co and S induce the formation of single-walled NT directly in the gas phase and prevent the NT tips from closing. Since sulfur itself does not catalyse the formation of NT, its role seems to reduce to the stabilisation of dangling bonds.

The addition of Bi and Pb also causes an increase in the NT diameter. The carbon ring structures formed in the gas phase are believed to play an important role in the mechanism of formation of single-walled NT. The most stable ring structures are those containing 10 to 40 carbon atoms, which form $C_{m}C_n$ clusters together with Co atoms. It is these clusters that function as catalysts, while S, Bi and Pb stabilise the ring structures.⁴¹

The results of studies on the catalysed arc synthesis of single-walled NT are summarised in Table 1.⁴² It can be seen that the diameter of NT obtained in this way varies from 0.6 to 6 nm.

Table 1. Characteristics of NT prepared by arc discharge synthesis in the presence of catalysts.⁴²

Catalyst	Diameter of NT /nm		Composition of crystallites ^a
	limits	average	
Fe	0.7–1.6	0.80, 1.05 ^b	Fe ₃ C
Fe	0.6–1.3	0.7–0.8	—
Co	0.9–2.4	1.3, 1.5 ^b	Co
Co	0.6–1.8	—	Co in a graphite shell
Ni	1.2–1.5	—	Ni in polyhedral particles
Ni	0.6–1.3	0.7–0.8	—
Fe + Ni	0.9–3.1	1.7	—
Fe + Ni	> 0.6	1.3–1.8	—
Co + Ni	> 0.6	1.2–1.3	—
Co + S	1.0–6.0	1.3, 1.5 ^b	Co and Co in polyhedral particles
Co + Bi	0.8–5.0	1.2, 1.5 ^b	—
Co + Pb	0.7–4.0	—	—
Co + Pt	~2	—	CoPt
Y	1.1–1.7	—	YC ₂ in polyhedral particles
Cu	1–4	—	Cu in polyhedral particles
None	> 2	—	—

^a The crystallites are located inside NT or polyhedral particles (see Section III.3). ^b The curve for the distribution of NT over diameters exhibits two maxima.

The mechanism of the catalytic action of metals in the formation of single-walled NT implies adsorption of carbon atoms on the surface of metal particles and their free migration over the surface to the base of a growing NT.⁴³ It was shown experimentally that the catalytic reaction can follow either of two routes, depending on the size of the metal catalyst particles. If the particle size (average diameter) is several tens of nanometers, which is much greater than the NT diameter (~1 nm), many closed NT sprout from one particle. If the particle size is not larger than the NT diameter, the particle moves together with the growing NT tip. The results of molecular dynamics modelling⁴³ confirmed the probability of the former pathway, involving migration of adsorbed carbon atoms to the NT base and the ‘root’ growth of NT. It should be borne in mind, however, that this model is of limited utility. It does not take into account the fact that NT formed in arc synthesis contain lots of defects and that a stream of carbon atoms directed towards growing NT has the greatest intensity near the NT tips. In addition, the conditions of vapour condensation in different sections of a setup, as well as in different setups are nonequivalent, which results in the formation of particles with dissimilar morphologies.

Nevertheless, the modelling made it possible to explain why multi-walled NT are not formed in the presence of catalytic additives (this would require cooperative processes, associated with consistent interaction of numerous particles), why single-walled NT always have relatively small diameters (the growth of NT is initiated on the surface bulges of metal particles and the diameter of these bulges is small with respect to the height), and why mixed catalysts are often more efficient than one-component ones (this is due to the enhancement of carbon adsorption, to the change in the activation energy of the NT growth, and to the formation of a surface with a large number of bulges).

Apparently, single-walled NT are even more prone to form bundles, which are combined in ‘ropes’ with a two-dimensional triangular crystal lattice.^{37, 44, 45}

Journier and Bernier,²⁶ who surveyed studies on catalytic arc synthesis, have rightly stated that the yield and the shape of NT can differ substantially even when the same metal is used, depending on the metal concentration, pressure of the inert gas, current strength (or density), and the geometry of the arc setup.

A special role in the arc synthesis of NT is played by boron, the introduction of which as B, B₂O₃ or BN induces the formation of a large number of well graphitised long (up to 20 µm) NT with boron-containing caps.⁴⁶ In this case, B₄C crystals, large fullerenes and BC₃ nanotubes are produced in addition to carbon NT. The presence of boron in the gas phase decreases appreciably the concentration of C₂ fragments in the plasma zone and the contents of fullerenes in the wall deposit.⁴⁷ Since the C₂ clusters are the main source of condensed structures, the introduction of boron can change the mechanism of the formation of NT. Note that the arc setup used in the study cited⁴⁷ differed only slightly in geometry and electric parameters from the conventional setups used for the synthesis of carbon NT [anode and cathode diameters 6 mm (a cathode with a diameter of 200 mm was also tested), distance between the electrodes 1 mm, current 80 or 150 A, voltage 25 or 40 V, respectively, gas pressure 27–67 kPa].

In some studies the formation of carbon NT, separate areas of which were made of BN has been noted.

Under certain conditions, for example, upon evaporation of BN or mixtures of B or BN with graphite, boron carbides, nitride, and carbonitrides can form 'self-contained' NT.^{48–51} The use of HfB₂ (see Refs 52, 53) or ZrB₂ (see 54, 55) electrodes for the electric arc synthesis in a stream of N₂ results in the formation of BN nanotubes. If BC₄N serves as the electrode material,^{56, 57} NT containing B, C and N (or BN) are produced; when the electrodes are made of graphite with the addition of BN,⁴⁸ the process yields NT containing BC₂N and BC₃. However, in the latter case, the composition of NT is nonuniform along the length of the tubes.

Unique multi-walled NT have been prepared by Suenaga *et al.*,⁵⁸ who also used HfB₂ and graphite as the electrode materials; several inner shells consisted of carbon, several central shells (embracing the carbon shells) were made of BN, and some outer shells were again carbon. The mechanism of formation of these NT (they evolved together with polyhedral particles, which also contained layers with different compositions) is totally unclear. The inner layers might grow upon diffusion from an NT tip; however, the probability of this process is low. Since the electronic properties of C and BN layers are different, this result brought about the idea of designing electronic devices with radial heterojunctions.

Studies on the catalytic synthesis have much in common with the studies on the synthesis of NT the inner cavity of which is filled with one or another substance.

3. Preparation of filled nanotubes

Filling of the inner cavity of NT (encapsulation) is a route to the development of a great number of novel nanomaterials of various classes and functions (materials with specific electronic, magnetic, optical, or mechanical properties, catalysts, sorbents). Some of them could be used as a type of 'NT–filler' nanocomposite, while other require that the carbon shell be removed (burned out). Particular attention is devoted to the preparation of 'quantum wires', *i.e.*, conducting materials with a diameter of several nanometers, whose conductivity is close to truly one-dimensional conductivity. The possibility of using NT and nano-rods in nanotechnological devices is being discussed.

The first study on filling NT was performed in 1993.⁵⁹ Mixtures of NT with Pb were annealed in air at ~400 °C. In the presence of O₂, the molten metal opened the tips of NT, removed the hemispherical caps and was sucked into the inner cavities of the NT by capillary action. However, it has been reported⁶⁰ that lead is able to fill NT only at pressures of 1000 to 10 000 atm; hence, under the conditions described above, NT were filled by lead compounds rather than by lead metal. Indeed, it has been shown that heating of a mixture of Pb₃O₄ with NT for 9 h at 700 °C results in opening and filling of the NT.⁶¹ Encapsulation of molten V₂O₅, PbO, Bi₂O₃ (see Refs 62, 63), MoO₃ (see Ref. 64) and AgNO₃ (see Refs 65, 66) into open NT has also been reported.

Even before the discovery of NT, the arc method has been used to prepare endohedral fullerenes⁶⁷ and nanoparticles encapsulated

into a multilayered graphite shells.^{68, 69} Therefore, it comes as no surprise that filling of NT can occur directly during the arc synthesis. Ordinary and filled NT are obtained under different conditions, in particular, filled NT are formed at lower temperatures (1000 to 2000 °C).

Yttrium carbide was the first substance detected inside NT prepared in an arc.^{70–72} According to an estimate,³⁵ yttrium is encapsulated into NT more easily than many other metals, although this feature can hardly be related to the enthalpy of formation of YC₂. Later, carbides of other lanthanides and Mn have also been encapsulated into NT.^{73–75} Carbides have been formed when metal-doped graphite anodes have been used because carbides are the species most stable in the presence of carbon. However, in some cases, elementary substances have also been detected inside NT, for example, Mn,⁷⁶ Cu, Ge^{77–79} and even small amounts of Y.⁷² These elements either do not form stable carbides or are liberated in an arc discharge under an H₂ atmosphere.

Thus copper forms no stable carbides and does not catalyse the formation of NT or fullerenes; therefore, the mechanism of its encapsulation differs from the mechanism of insertion of other metals.⁷⁸ Evaporation of a graphite anode in a hydrogen plasma in the presence of copper gives rise to polycyclic aromatic hydrocarbons, which form graphite shells around Cu particles.^{78, 79} The formation of filled NT upon joint evaporation of pyrene and Cu or Ge (this was done using a Cu anode with a cavity filled with pyrene and a W cathode)⁸⁰ was considered^{78, 79} as direct evidence supporting the above statement.

Metals with different volatilities show different behaviour during encapsulation.⁸¹ Some substances fill long NT giving continuous crystals with lengths of up to 1 µm (Cr, Ni, Sm, Gd, Dy, Yb, S, Se, Ge, Sb); other substances fill only short NT (Al, Bi, Te), and some other elements form inclusions separated from one another inside NT (Co, Fe, Pd).^{36, 82–85} In a study of encapsulation of high-melting transition metal carbides (NbC, TaC, MoC), an exceptionally stable face-centred form of the carbide MoC was discovered.⁸⁵ Nanotubes containing B₄C in the inner cavity have also been prepared.⁸⁶

The operation conditions used in these studies^{70–83} did not differ much from those used for the synthesis of NT. Thus Setlur *et al.*⁷⁸ used electrodes with a diameter of 10 mm located at a distance of 0.25 to 2.0 mm; the current was 100 A, the voltage was 20 V and the gas pressure ranged from 1.3 to 6.7 kPa. In another series of studies,^{82–84} the corresponding parameters were 9 mm, 1 mm, 100–110 A, 20–30 V and 60 kPa.

Sulfur plays a special role in the formation of filled NT.⁸⁴ Sulfur can be contained in a graphite anode as a minor impurity; it promotes filling of NT with other elements. In some cases, sulfur enters NT as a sulfide but more frequently it is not present in the filling material. This effect of sulfur has been explained⁸⁴ by the fact that sulfur forms clusters with carbon in the gas phase; this ensures transportation of sulfur to the growing NT, where it promotes graphitisation of NT and reconstruction of a metal surface, resulting in the exposure of catalytically more active crystallographic planes. At the final stages of the process, sulfur is removed from the graphite shell of the NT. These results are similar to the data reported in earlier publications.^{39, 40} In some cases, sulfur suppresses the formation of single-walled NT.

The technique of filling NT under the conditions of arc synthesis suffers from a severe drawback — this process is hardly controllable. The yield of filled NT and the composition, structure and morphology of encapsulated substances cannot be governed in the majority of cases.

4. Modifications of arc synthesis

The use of an alternating-current arc and electrodes with identical diameters changes substantially the pattern of the process, namely, the products are formed on the chamber walls rather than at the electrodes, new forms of NT being produced together with the known ones.^{87, 88} The yields and forms of some products

also depend on whether the electrodes are mounted in the vertical or horizontal position.

A series of publications^{19, 89–91} deal with the formation of multi-walled NT under a methane atmosphere. This process differs from the conventional one (performed under an inert gas) in the fact that, under some conditions, the formation of NT is not accompanied by evolution of fullerenes or nanoparticles. At high partial pressures of methane, relatively thick multi-walled NT are formed and at low pressures (1–3 kPa), thin and long multi-walled NT are produced. The optimal conditions for the formation of thin NT for the vertical mounting of electrodes with a diameter of 6 mm are the following: methane pressure 2.7 kPa, current 30 A.

Later, the authors of the above series of studies arrived at the conclusion that, since CH₄ decomposes in an arc to give C₂H₂ and H₂, the synthesis of NT should better be performed in a stream of H₂ (see Refs 92–95).[†] Some advantages of using H₂ have been mentioned above in the consideration of copper encapsulation. A certain role in the formation of NT can also be attributed to the high heat capacity of H₂, owing to which it can efficiently quench NT.⁹⁶ When the process is performed at 'plasma' temperatures, the fact that the energy of ionisation (the first ionisation potential) of H₂ is half that of He also becomes significant.

Rather long NT are formed even at an H₂ pressure of 7 kPa; their yield at a pressure of 13 kPa is comparable with the yield attained in the atmosphere of He at 66 kPa. Many NT prepared in a flow of H₂ have a narrow inner channel; they are open and usually high-quality NT (having few nanoparticles on the outer surface). The thinnest and longest multi-walled NT were prepared at H₂ pressures of 6.7–11 kPa.

The arc synthesis in an atmosphere of H₂ differs appreciably from the synthesis in inert or hydrocarbon media because the temperature developed in the atmosphere of H₂ is higher. This provided grounds for assuming that C⁺ ions participate in the formation of NT in an H₂ medium.⁹² It is also assumed that either H₂ molecules or H atoms add to the dangling bonds of growing NT and thus prevent closure of these bonds and, in addition, eliminate the possibility of the formation of amorphous carbon.⁹² The addition of H₂ is evidenced by the fact that an increase in the partial pressure of H₂ results in higher yields of open NT. The mechanism involved may be similar to the mechanism of the formation of diamond from the gas phase. Particles of various natures are produced; however, under a hydrogen atmosphere, the most reactive ones are completely or partially gasified (etched).

Yokomichi *et al.*⁹⁷ have attempted to prepare NT in a CF₄ medium. It has been assumed that the F atoms formed upon decomposition of CF₄ would attach to the dangling bonds and prevent them from closing, thus influencing the process of NT formation. This assumption largely proved to be correct; in any case, no fullerenes were formed together with NT. The synthesis was carried out using a setup with electrodes 5 mm in diameter at a current of 20–60 A and a CF₄ pressure ranging from 2.7 to 53 kPa. Under the optimal conditions (20–40 A, 6.7–13.3 kPa), multi-walled NT were synthesised with an outer and inner diameters of 20 and 5 nm, respectively; they did not differ much from the NT obtained in a flow of He.

The researchers cited⁹⁷ studied the influence of the main parameters of the process (medium, gas pressure and current) on the yield of NT and polyhedral particles and on the length of NT and compared their data with those reported in other publications; the results were summarised in a table (Table 2). In particular, it follows from this table that the processes occurring in an atmosphere of CF₄ and CH₄ are fairly similar. However, the data of Table 2 should be treated with caution because this way of presenting the information does not show, for example, that in

Table 2. Influence of the increase in the gas pressure and in the current on the main characteristics of electric-arc synthesis of NT under atmospheres of various gases.⁹⁷

Medium	Yield of NT	Length of NT	Yield of nano-particles
CF ₄	decreases	increases	decreases
He	increases	does not change	does not change
CH ₄	decreases	increases	does not change
H ₂	decreases	does not change	does not change

some cases, the plots for the variation of the yield vs current pass through a maximum.

Koprinarov *et al.*⁹⁸ have attempted to devise a continuous electric arc process and to make up for the consumption of graphite due to evaporation by supplying CH₄. For this purpose, they used the 'reverse method', *i.e.* the area of the anode in the setup used was an order of magnitude greater than the area of the cathode. The products of electric-arc synthesis were found to contain fullerenes, polyhedral particles and single-walled and multi-walled NT. The nanotubes had different lengths and structures. Some of them were partly single-walled and partly multi-walled structures; this indicates that various sections of NT grew at different rates. The 'reverse method' offers no advantages over the conventional method.

Carbonised coal can be used as the electrode material instead of graphite;⁹⁹ however, the presence of non-volatile impurities causes contamination of NT; hence, in the majority of studies, high-purity graphite is the material of choice.

The main drawback of the arc method is low output. This is demonstrated by a publication³⁷ in which synthesis in a He flow in the presence of Ni and Y introduced in a graphite anode gave only 2 g of NT over a period of 2 min. After that, the setup had to be disassembled to replace electrodes and take the products out.

III. Laser-assisted synthesis

Fullerenes were first obtained by the laser method in 1985; however, only 10 years later, this method was employed to prepare NT.^{100, 101} The first setup was a 50-cm quartz tube with a diameter of 2.5 cm containing a graphite rod 1.25 cm in diameter arranged along the tube axis. The tube was evacuated and simultaneously heated to 1200 °C. After that, Ar was supplied (pressure 66.5 kPa, linear gas velocity 0.2–2.0 cm s^{−1}). The target was exposed to a laser beam with a wavelength of 532 nm (Nd laser), a pulse frequency of 10 Hz, a pulse power of 250 mJ, and a pulse duration of 10 ns. The surface of the target was scanned by a laser spot with a diameter of 3 or 6 mm. The products of evaporation (multi-walled NT and nanoparticles) were collected on a cooled copper finger, on the walls of the tube, and on the reverse side of the graphite target (Fig. 5).

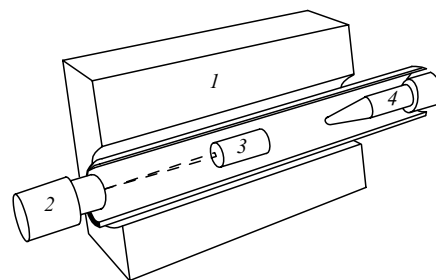


Figure 5. Scheme of the laser setup; (1) furnace heated to 1200 °C; (2) neodymium laser; (3) graphite target; (4) water-cooled collector.

[†] Subsequently, the same conclusions have been drawn by other investigators.⁹⁶

The daily output of the first setup was up to 80 mg of a nanomaterial containing NT. The process had to be terminated because the tube was clogged near the target with a web-like material which also contained NT. By using a tube with a diameter of 3.8 cm, all other conditions remaining almost the same, another group of researchers attained a higher yield of a rubbery material containing single-walled NT. In this case, the output was 200 mg per experiment (3–5 h).¹⁰² It was noted that distribution of the NT over diameters depends on the radiation wavelength (either 532 or 1064 nm).¹⁰²

An increase in the diameter of the reaction tube to 5 cm was even more effective. This setup can afford ~ 1 g of the material (containing 60%–90% of NT) per 24 h.¹⁰³

Subsequently, one laser was replaced by two lasers (wavelengths 532 and 1064 nm), which emitted alternately, the interval between the pulses being 42 ns, and the power of a pulse was increased to 490 and 550 mJ, respectively.¹⁰³ This made it possible to ‘knock down’ the plums formed. Subsequently the tube diameter was doubled once again; in addition, alternation of the side of the target exposed to radiation and beam scanning were used. As a consequence, the yield of products containing 40%–50% of NT reached 20 g during 48 h of continuous operation.¹⁰³

Yudasaka *et al.*¹⁰⁴ used a modified setup with two targets, one made of a graphite powder and the other made of a metal or an alloy.

Study of the influence of the pressure of Ar and the furnace temperature on the yield and properties of the laser ablation product has shown that at pressures below 13 kPa only amorphous carbon is formed, while NT appear in the products, together with amorphous carbon, above 26 kPa.¹⁰⁵

An increase in the furnace temperature from 780 to 1050 °C resulted, in the presence of catalysts, in an increase in the average diameter of single-walled NT from 0.8 to 1.51 nm, although the yield of NT at low temperatures was relatively low.¹⁰⁶

The yield and the shape of NT prepared by the laser method are determined by fewer parameters than those of the NT obtained by the electric-arc synthesis. Perhaps, this is why markedly higher yields of NT have been attained in the laser-assisted synthesis. The temperature of the area from which graphite is evaporated and the temperature gradient in the gas phase near this area can be considered to be the crucial factors. Unfortunately, in the experiments described above these parameters have been determined insufficiently definitely if at all (the measurements were hampered by the beam scanning over the target surface). Instead, properties influencing the temperature of evaporation were measured (the furnace temperature, laser radiation power, diameter of the light spot on the target, the velocity of the spot migration, the gas pressure, and the gas flow rate).

The introduction into graphite of small amounts of catalysts led to the formation of single-walled NT, which, unlike those obtained in arc, were only slightly covered by amorphous carbon particles.^{101, 107} Mixtures of Co with Ni (0.6 at.% each) and of Co with Pt (0.6 at.% and 0.2 at.%) proved to be the best catalysts. When these mixtures were used, the yield of single-walled NT exceeded 70%, which is tens or hundreds times higher than the yields attained using individual metals as the catalysts. High yields have also been obtained with mixtures of Ni with Pt.¹⁰⁰

The use of a mixture of two noble metals, Rh and Pd, mixed with graphite in a laser-assisted synthesis afforded single-walled NT with diameters of 1.0–1.5 nm.¹⁰⁸ Only mixtures of Cu with Ni were found to be substantially less active than copper itself.¹⁰⁰

The mechanism of the catalytic formation of single-walled NT upon laser ablation proposed by Thess *et al.*¹⁰⁷ was defined as the ‘scooter’ mechanism. According to this mechanism, individual atoms of Ni, Co or other catalytically active metals are adsorbed on the open tips of the curved C_n ($n \leq 50$) graphene fragments and ‘scoot’ around the tips, thus promoting removal of all carbon structures except for the energetically preferred ones.

Clusters comprising 10 to 100 closed-tip nanotubes formed ‘ropes’, 10 to 50 of which composed bundles. A more detailed study of the ‘ropes’ showed that they are polycrystals, the sizes of separate grains ranging from 10 to 100 nm (the typical size is 10 to 20 nm); their cross-sections are oval and the predominant aspect ratio is ~ 3 .¹⁰⁹

Some of the NT are clustered into 5–15 nm thick ‘ropes’ forming rings with diameters of 300–500 nm.¹¹⁰

The products of laser-assisted synthesis were found to contain an interesting type of NT, so-called ‘nano-peas’, which are chains composed of spherical C_{60} molecules located inside single-walled NT with a diameter of 1.3–1.4 nm.¹¹¹

The laser method also makes it possible to prepare NT from BN;^{112–115} however, the experimental conditions employed in this case differed sharply from those used to prepare carbon NT; specifically, high and superhigh pressures were used. The process induced by laser heating of hexagonal BN in a diamond anvil at a high pressure under an atmosphere of N_2 has an interesting feature, namely, cubic BN appears at the bottom of the NT formed.¹¹⁵ The mechanism of formation of NT from BN upon laser evaporation at superhigh pressures might include a stage of surface diffusion of molecules from the bottom of an NT to its tip, which implies restriction of the NT length.¹¹⁶

Laser ablation of a complex target (C, Si, BN) at near-atmospheric pressure accompanied by chemical reactions can be used to synthesise axial NT. This type of NT with diameters of several tens of nanometers and with lengths of up to 50 mm contained a core of β -SiC, an intermediate layer of amorphous SiO and an outer shell of BN and C.¹¹⁷ The study cited aimed at designing coaxial nano-sized electronic devices with heterojunctions.

In addition to the neodymium laser, a CO_2 laser has also been tested for the synthesis of carbon NT.¹¹⁸

IV. Other methods of graphite vaporisation

The conclusion that fullerenes and NT are formed in the vapour phase, irrespective of the way used to vaporise graphite or another form of carbon, was drawn fairly long ago and has been confirmed in a number of publications. Thus Ebbsen *et al.*¹¹⁹ proved, using isotope dilution, that NT (as well as fullerenes) are formed exactly from carbon vapour. Apart from the arc- and laser-induced evaporation of graphite considered above, NT are also prepared using resistivity vaporisation and vaporisation induced by electron or ion beams or by sunlight.

1. Resistivity vaporisation

Heating a 0.5-mm graphite foil by Joule heat *in vacuo* (10^{-6} Pa) and cooling the resulting vapour to -30 °C resulted in NT being deposited on the surface of single-crystalline graphite.^{120–123} The rate of deposition of NT with a diameter of 1–4 nm was 0.5 A s^{-1} . The NT were capped and combined in arrays. This method permits the preparation of particles having diverse shapes — single-walled and multi-walled NT, NT bundles and nano-cones, the yield of single-walled NT ranging from several percent to 80%–90%.

2. Electron- or ion-beam vaporisation

The first experiments on the preparation of NT by electron-beam vaporisation of high-purity (99.99%) reactor grade graphite *in vacuo* (10^{-3} Pa) and deposition on various substrates (Si, quartz, graphite, ceramics, anodised Al) were performed in Russia back in 1992.¹²⁴ The resulting condensate was a 0.01–10- μm thick film consisting of NT with a diameter of ~ 1 nm. Separate NT were joined in fibres ~ 5 nm in diameter, while the fibres were clustered in cables with a diameter of 10–30 nm. The tubular texture was retained throughout the whole film thickness; moreover, variation of the angle between the direction of the stream of carbon particles and the substrate surface resulted in the formation of inclined

textures. Kosakovskaya *et al.*¹²⁴ measured a large number of film characteristics and noted anisotropy of film properties.

Nanotubes have also been formed on bombardment of high-purity graphite with Ar^+ ions with an energy of 60 keV in a high vacuum at a normal angle of incidence.¹²⁵ Polyhedral nanoparticles were isolated together with NT.

Exposure of hexagonal BN to an electron beam gave NT;¹²⁶ as in the study described above,¹¹⁵ in this case, too, the formation of seeds of cubic boron nitride at an initial stage was assumed. The irradiation with electrons with a current density of $10\text{--}20\text{ A cm}^{-2}$ at a voltage of 300 kV resulted in annealing of most of defects and in almost complete ordering of the BN walls of the NT.¹¹² An electron beam with a current density of 150 A cm^{-2} at an accelerating voltage of 400 kV ensured the formation of multi-walled coaxial BN clusters.¹²⁷

Irradiation of boron-containing carbon with electrons gave carbon NT doped with boron.¹²⁸

The role of the gas phase in this process and in other processes described above is obscure; therefore, the term 'vaporisation' is used only conditionally.

3. Sunlight-induced vaporisation

The studies dealing with the use of solar concentrators for the preparation of NT have been briefly surveyed in a publication.²⁶ These studies were carried out only in France. A setup producing a temperature of about 3000 K at the focus was developed. Evaporation of pure graphite gave only a small amount of soot, whereas vaporisation of a graphite powder with catalysts gave rise to NT. The type of NT formed (single-walled, multi-walled or bamboo-like) and the amount of impurities were governed by the catalyst and the gas pressure in the process, *i.e.*, by the same parameters as in the case of electric-arc and laser-assisted syntheses, described above and studied much more extensively. In the presence of Co, single-walled NT with a diameter of 1–2 nm were found in the soot deposit and NT bundles with diameters of more than 20 nm containing no admixture of amorphous carbon were found in the web-like deposit.

V. Pyrolysis of hydrocarbons and decomposition of CO

1. Catalytic pyrolysis

Catalytic pyrolysis of hydrocarbons had been used to prepare carbon fibres even before the discovery of NT and fullerenes. Nanotubes were first synthesised by this method in 1993.¹²⁹ The course of the process is influenced by the temperature, the overall pressure, the initial hydrocarbon used and its partial pressure, the nature and characteristics of the catalyst (first of all, the particle size, which could determine the diameter of the NT), and the nature of the catalyst support. The pyrolysis can result in layers of amorphous carbon or graphite formed around catalyst particles, carbon fibres and multi-walled or single-walled NT.²⁶ The length of NT and the degree of their coverage by amorphous carbon particles depend on the duration of the process.

a. Pyrolysis of acetylene

Acetylene is used most often for pyrolysis. José-Yacamán *et al.*¹²⁹ carried out acetylene pyrolysis at 500 °C and atmospheric pressure over a graphite catalyst containing 2.5% of Fe. The concentration of acetylene in the diluent (N_2) was 9%. It was noted that graphite particles are formed initially around the Fe particles and this is followed by growth of NT with diameters of 5–20 nm and lengths of up to 50 μm . Nine different catalysts (Fe, Co, Ni and Cu supported on three materials — flake graphite, SiO_2 or HY zeolite) have been assayed;^{130, 131} the effects of the flow rate, the temperature and duration of the pyrolysis on the yield and quality of NT have been studied. An increase in the temperature from 500 to 800 °C influences only slightly the length of NT but increases the yield of amorphous carbon (amorphous carbon constitutes up to 50% of the deposit even under the optimal conditions). Longer

pyrolysis times result in higher relative yields and greater lengths and diameters of NT. The replacement of the inert diluting gas by H_2 barely influences the growth of NT. In all cases, the structure of NT was defective. A graphite coating was formed around the catalyst particles and multi-walled NT were 'extruded' from it.

Testing of Fe catalysts prepared by various procedures showed¹³² that Fe supported on SiO_2 provides the best results. The greatest yield of NT was attained when C_2H_2 was pyrolysed at 700 °C. The outer and inner diameters of NT were, on the average, 10–20 and 5–8 nm, respectively.

As a further development of the study cited,¹³² pyrolysis of C_2H_2 over Fe particles in mesoporous SiO_2 has been carried out.¹³³ The catalyst was prepared by hydrolysis of tetraethoxysilane in a solution of $\text{Fe}(\text{NO}_3)_3$ followed by reduction with an $\text{H}_2\text{--N}_2$ mixture at 550 °C. The diameter of NT ($\sim 30\text{ nm}$) obtained at 700 °C from an acetylene–nitrogen gas mixture (9% of C_2H_2) was nearly equal to the diameter of pores in SiO_2 . It has been assumed that NT with a smaller diameter can also be obtained in this way. Each NT contained 40 to 50 shells and was located at a distance of $\sim 100\text{ nm}$ from the closest neighbours; thus, the deposit looked like a 'forest' consisting of nanotube 'stems' parallel to one another. The rate of the growth of NT was about $25\text{ }\mu\text{m h}^{-1}$. In the initial stages, NT were free from the amorphous carbon impurity; however, as the duration of the pyrolysis and, correspondingly, the length of NT increased (the NT grew to a length of 50–100 μm over a period of 2–5 h), the 'stems' bent and amorphous carbon appeared on their surface. The main obstacle hampering the conducting of larger-scale process is the difficulty of manufacturing substrates with large dimensions because they are subject to shrinkage and cracking.

An improved method for the synthesis of a supported Fe catalyst has been proposed.^{134, 135} The method was based on the deposition of a film of a $\text{Fe}(\text{NO}_3)_3$ -containing gel onto a 30–50 μm quartz plate, the removal of excess water and other solvents and drying at 80 °C. As this was done, the gel cracked into pieces with an area of 5–20 mm^2 each. These pieces were calcined *in vacuo* and then the iron was reduced to give small (5–50 nm) iron particles distributed uniformly over the surface.

Pyrolysis of a $\text{C}_2\text{H}_2\text{--N}_2$ mixture containing 9% of acetylene at 600 °C and a pressure of 24 kPa in the presence of this catalyst made it possible to obtain NT in very high yields. The outer diameter of NT amounted to 30–40 nm and the inner diameter was 10–15 nm. They consisted of 10–30 coaxial layers. Individual NT were located at distances of $\sim 100\text{ nm}$ from one another. The rate of the growth was $30\text{--}40\text{ }\mu\text{m h}^{-1}$ and the length of NT (attained in 48 h) was $\sim 2\text{ mm}$. The greatest area coated by NT was 15 mm^2 . No formation of polyhedral particles was detected. The layer of NT was easily separable from the substrate.

A mechanism consisting in the NT growth on the side of a free tip, which is covered by a catalyst particle, has been proposed for this process.¹³⁵ The micrographs of NT obtained by the transmission electron microscopy, which are presented in a study cited,¹³⁵ show an iron particle at the tip of the NT and a top-shaped cavity at the NT base. These results are at variance with the data of José-Yacamán *et al.*¹²⁹ It has been considered initially that the reaction mechanism should include the formation and decomposition (upon supersaturation) of 'active' metal carbides. This mechanism was consistent with the fact that the growth of NT, which has stopped after cooling of the carbonised catalyst, is resumed after the subsequent heating. The root growth of NT can proceed by a mechanism described previously and assuming the surface diffusion of carbon atoms to the bulges on the catalyst surface;⁴³ in this case, dehydrogenation of C_2H_2 on the catalyst surface to give H_2 rather than mere adsorption of carbon can be the first stage of pyrolysis. A mechanism involving immersion of small C_n clusters into the caps of NT has also been considered. It should be stated that catalytic pyrolysis of the same hydrocarbon (C_2H_2) present in the same concentration in N_2 (9%) at similar temperatures (500 and 600 °C) can follow absolutely different

mechanisms depending on the pressure in the system, the method used to prepare the catalyst and other factors.

Pyrolysis of C_2H_2 over Fe-containing catalysts supported on various materials including SiO_2 has been considered in several other publications.^{136–139} It was noted that, in addition to the NT described above, helical and even branched NT can be formed.

Apart from iron, cobalt also exhibits high activity in the pyrolytic decomposition of C_2H_2 .¹³⁶ The materials used as supports for this metal include SiO_2 ,^{137, 140, 141} NaY zeolite¹³⁷ and Al_2O_3 .¹⁴² The procedure for the preparation of Co catalysts, in particular, the pH of precipitation of the metal salt from a solution, influences appreciably the quality of NT.¹⁴¹ Biro *et al.*¹⁴³ have classified NT into two groups: 'raft-like arrays' with a diameter of 1 nm and single ones with a diameter of 10 nm. Remarkable NT with a coil structure were also isolated upon pyrolytic decomposition of C_2H_2 over Co.

Nanotubes of this type have been studied in detail.¹⁴⁴ It was shown by high-resolution electron microscopy that the coils consist of several straight sections, the junctions of which can contain disordered areas. The convolutions closely adjoin one another, the NT forming them being 'flattened', *i.e.* compressed along the coil axis.

A certain catalytic activity in the formation of NT from C_2H_2 is displayed by Ni and Mn oxides, while platinum metals proved to be poor catalysts.¹³⁶ However, a catalyst promoting the formation of very long NT was prepared from $Pt_5(CNC_8H_9)_{10}$.

Catalyst particles can be introduced into a support by impregnating it with aqueous solutions of salts followed by decomposition of the salts, by chemical vapour deposition using organometallic compounds, or by electrodeposition. The size of metal particles can range from several nanometers to tens of nanometers.

Zeolites, especially NaY zeolite, make good supports for the catalysts of acetylene pyrolysis.¹³⁷

The synthesis described in Refs 133–135 should actually be categorised as a template synthesis. Membranes prepared by anodic oxidation of Al are also good templates for the catalytic synthesis of NT.¹³⁹ These membranes contain parallel closely packed hexagonal channels (pores) running throughout the whole bulk. By varying the conditions of anodic treatment, one can control the pore diameter (2–500 nm), the membrane thickness (50–500 nm) and the pore density (10^7 – 10^{12} cm⁻²). The Al_2O_3 membranes are transparent and stable up to a temperature of at least 1000 °C; the chemical properties of their surface can change upon the addition of hydroxy groups.

Recently a template synthesis of NT by pyrolysis of C_2H_2 in the presence of a mixed catalyst has been performed.¹⁴⁵ Commercial zeolite samples were impregnated with aqueous solutions of Co and V acetates and used in the process immediately after drying. The pyrolysis was carried out at 700 °C. This procedure yielded well graphitised and relatively thin NT (10–12 shells, outer diameter 8–10 nm, inner diameter 2.5–2.8 nm). The role of the vanadium additive is unknown; the mechanism proposed in the study cited¹⁴⁵ and involving the transition of metal compounds to the gas phase seems doubtful.

b. Pyrolysis of methane, ethylene and propylene

It has been noted in a publication¹³⁷ devoted to the pyrolysis of acetylene that the use of methane, ethylene or propylene instead of acetylene either does not give NT or gives them in low yields. However, in some studies, conditions have been selected under which pyrolysis of these compounds does yield NT. Thus a deposit consisting of NT to an extent of 90% was obtained from CH_4 at 600 °C in the presence of the $Ni_xMg_{1-x}O$ catalyst, prepared from Ni and MgO, in which some Ni atoms were located on the catalyst surface as aggregates.^{146, 147} The synthesis of NT with a length of > 20 μm from a CH_4 – H_2 mixture in the presence of Fe particles has been reported.¹⁴⁸ An interesting point in this study¹⁴⁸ is that NT were synthesised using a microwave setup (Fig. 6), widely employed for the preparation of diamond films. However, the

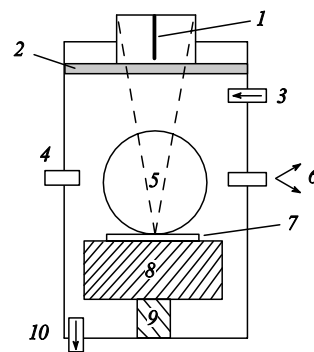


Figure 6. Setup for plasma-activated chemical deposition from the gas phase. The pressure of the mixture of CH_4 and H_2 at the inlet is 0.13 Pa, the substrate temperature is 370–950 °C; (1) microwave antenna; (2) quartz window; (3) gas inlet; (4) viewing window; (5) plasma discharge; (6) to the optical emission spectrometer; (7) substrate; (8) an energy-sensitive graphite stand; (9) drive to a stepper motor; (10) to a vacuum pump.

synthesis of single-walled NT carried out at Stanford University (USA) appears the most impressive.^{149, 150} In this study, methods of nanotechnology were employed. The catalyst was applied to a silicon plate as micron-sized islets. To this end, square holes were made in a poly(methyl methacrylate) film by electron-beam lithography and then the catalyst precursor was deposited onto the film from a methanol solution containing $Fe(NO_3)_3$, $MoO_2(acac)_2$ and Al_2O_3 particles. Subsequently the solvent and the film were removed, the catalyst was heated in argon, and, finally, pyrolysis of CH_4 was carried out.

During pyrolysis, very straight NT with diameters of 1–3 nm and lengths of up to 20 μm containing no topological defects were formed on the catalyst islets over a period of 10 min. Some NT served as bridges between neighbouring catalyst islets and thus formed electric contacts. An increase in the process duration to several hours resulted in thicker NT.

This method is rather straightforward and easily reproducible; it can be used to prepare NT on substrates having large areas.

The $CoSi_2$ formed upon the deposition of cobalt onto silicon also catalyses the formation of NT from CH_4 .¹⁵¹

The use of ethylene for the template catalytic synthesis of single-walled NT on porous Al_2O_3 plates has been described.^{152, 153} Pyrolysis of propylene^{132, 137, 139} and pyrolysis of polyethylene over a Ni catalyst have been reported.^{154, 155}

c. Pyrolysis of benzene and other aromatic compounds

Benzene can also serve as the initial hydrocarbon for the synthesis of NT; this synthesis can be carried out using the equipment designed for the preparation of carbon fibres from C_6H_6 .¹⁵⁶ It was noted that the growth of NT and carbon fibres follow different mechanisms; indeed, catalyst particles were detected at the tips of the fibres, whereas the NT usually had conical caps free from inclusions. The preparation of NT from a C_6H_6 – H_2 mixture over an Fe catalyst requires as a rule lower partial pressures of C_6H_6 and lower temperatures than the synthesis of fibres. In some cases, the growth of NT is replaced by the growth of solid fibres. Solid fibres and NT prepared from the same hydrocarbon in single-type equipment differ markedly in mechanical properties — the fibres are easily broken on bending, whereas NT exhibit flexibility and elasticity.

Pyrolysis of C_6H_6 over Co supported on SiO_2 affords simultaneously bent and helical NT and fibres,¹⁵⁷ the ratio of the yields of NT and fibers being determined by the size of the catalyst particles and the composition of the reaction mixture. A catalyst containing a higher proportion of Co (5 mass %) and consisting of larger particles (11 nm) results in a higher proportion of fibres than a catalyst with a lower metal content (0.5 mass %) and a

medium particle size (7 nm). The replacement of the gas diluent H_2 by N_2 increases the yield of NT.

The helical NT resulting from the pyrolysis of C_6H_6 differ from those formed upon the pyrolysis of C_2H_2 (see above¹⁴⁴); they are multi-walled NT, the distance between the shells being intermediate between the corresponding distances in ordinary and turbostratic graphites. The shells themselves are largely disordered.¹⁵⁷ Among other reasons, the formation of such structures might be due to the addition of hydrogen (the diluent of benzene) to the dangling bonds of NT. However, the catalyst particles exert a greater influence. This hypothesis is consistent with the model proposed by Amelinckx *et al.*,¹⁵⁸ which assumes that the growth of NT progresses on the side of a free tip having an encapsulated catalyst particle.

Deposits of NT with a definite texture can be obtained from gaseous C_6H_6 . Thus pyrolysis of C_6H_6 on a profiled substrate with scratched parallel grooves gives rise to NT arranged parallel to the substrate surface and growing from the upper edges to the centres of the grooves.¹⁵⁹ It was suggested that irregularities on the upper edges of the grooves exhibit enhanced catalytic activity.

A similar expedient has been used in the pyrolysis of 2-amino-4,6-dichloro-*s*-triazine.^{160,161} A 10- to 100-nm thick Co film was sprayed onto a SiO_2 plate. Then 1 to 20 μm wide tracks spaced 100–200 μm apart were etched on the substrate using a laser. The substrate was placed in a furnace the coating downwards and pyrolysis was carried out at 950 °C. This gave rise to NT bundles having a strictly identical length and very close outer diameters (30–50 nm). The NT obtained in this way contained up to 5% of nitrogen. When the plate was placed in the furnace the coating upwards, the situation changed sharply; strongly twisted NT were formed.¹⁶¹ This outcome has not yet been adequately interpreted.

The researchers believe that etching of the Co film gives rise to energy-saturated metal or metal oxide clusters, which are deposited along the track edges. Hydrogen chloride, arising upon decomposition of triazine, can convert Co into volatile $CoCl_2$ and thus influence the catalytically active particles at the tips of NT. The growth of NT is terminated when the catalyst species have lost activity or have been completely evaporated as the chloride.

Pyrolysis of tris(aminotriazine) (melamine) and cyanuric acid over etched Co, Ni, or Fe films occurred in a similar way.

A mixture of gaseous phenylacetylene and thiophene with He¹⁶² and a mixture of 2-methyl-1,2'-dinaphthyl ketone with He¹⁶³ in the presence of a Ni catalyst have also been used for the pyrolytic synthesis of NT. It is noted in both studies that at the first stage of pyrolysis, Ni particles are coated with a graphite layer; this is followed by the nucleation and growth of NT. The temperature of choice is 700 °C. Yudasaka *et al.*¹⁶³ proposed an original procedure for the preparation of the catalyst. They sputtered a metal film on a quartz glass substrate and heated it *in vacuo*. The size of the Ni particles thus formed was determined by the thickness of the deposited film; in the optimal case, it was 20–30 nm. It has been concluded¹⁶² that NT are 'extruded' from Ni_3C particles; Yudasaka *et al.*¹⁶³ noted an important role of the shape of Ni nanoparticles.

2. Pyrolysis in the presence of a 'floating catalyst'

A conventional supported catalyst is coated, sooner or later, by a layer of the products of pyrolysis of hydrocarbons and is thus deactivated. The introduction into the system of catalyst precursors as volatile compounds which decompose to give catalytically active species directly in the reaction area could, in principle, permit one to avoid the catalyst deactivation and to bring the process of pyrolysis closer to a continuous process.

There are only a few publications in which this approach has been employed. Thus decomposition of Ni phthalocyanine at 700 and 800 °C has resulted in the synthesis of NT containing some nitrogen.¹⁶⁴ These NT were multi-walled particles with large (~200 nm), small (10 nm) or variable diameters, their length reaching 6 μm . It has been assumed¹⁶⁴ that the mechanism of

the NT growth includes encirclement (encapsulation) of Ni particles with a carbon layer, graphitisation of this layer, the change in the shape of Ni particles, the appearance of seeds and the growth of NT. The Ni particle inside the NT can either migrate from the substrate to the growing tip or remain in a particular section of the NT, forming a node point.

Decomposition of Fe and Co phthalocyanines is also accompanied by the formation of NT, whereas Cu phthalocyanine gives neither NT nor graphitised particles.

Ferrocene has been used as the 'floating catalyst' in the pyrolysis of thiophene.¹⁶⁵ Unlike the study cited above,¹⁶⁴ in this case, single-walled NT were produced. The process was carried out at 1100–1200 °C for 1 to 30 min. This yielded a large amount of long and relatively thick 'ropes' and ribbons coloured silvery black. Some of the ribbons were semitransparent and not attached to the surface. The longest 'ropes' were 3–4 cm long and had a diameter of 0.1 mm, while the ribbons were up to several millimeters wide. Each 'rope' and each ribbon consisted of several thousands of vaguely oriented threads, comprised by bundles of well oriented closely packed single-walled NT. The diameter of the bundles ranged from several to forty nanometers, the average diameter of the NT being 1.7 nm. It was found that the bundles are formed in the reaction area and carried away with the gas stream; outside the area they stick together forming 'ropes' or ribbons.

Pyrolysis of ferrocene and its mixtures with C_2H_2 has also been studied.¹⁶⁶

3. Decomposition of CO

Thermal decomposition of CO (disproportionation to CO_2 and carbon) differs sharply from the pyrolysis of hydrocarbons from the thermodynamic viewpoint; at atmospheric pressure and low temperatures (300–750 K), the equilibrium yield of carbon is nearly quantitative, while at higher temperatures and lower pressures, it diminishes. Conversely, the yield of carbon in the pyrolysis of C_2H_2 and CH_4 increases as the temperature rises and the pressure is reduced and approaches a quantitative yield at 1250–1500 K.

In this respect, carbon monoxide may seem to be a less convenient starting compound for the synthesis of NT. However, for kinetic reasons, a hydrocarbon is more difficult to heat to a temperature above 800–900 °C (before it is brought in contact with the catalyst) than CO; hence, carbon monoxide offers some advantages.

The first study¹⁶⁷ on the catalytic decomposition of CO to give NT was carried out in 1995, *i.e.* much later than NT were synthesised by other methods. Decomposition of a CO– CO_2 gas mixture (20% of CO) was carried out at 500 °C over the Ni/Al_2O_3 catalyst. A graphitised shell was formed around the Ni particle; nanotubes protruded out of this shell. The introduction of hydrogen into the gas mixture changed appreciably the morphology of the deposit.

Thermal decomposition of neat CO over a Ni–Co catalyst supported on Al_2O_3 was performed at 1200 °C at a pressure somewhat higher than atmospheric.¹⁶⁸ This process gave rise to single-walled NT.

The preparation of an active molybdenum catalyst used for the synthesis of NT from CO was an important achievement. The catalyst was prepared by impregnation of alumina with a methanol solution of bis(acetylacetonato)dioxomolybdenum followed by heating to 200 °C. The diameter of NT formed in the presence of this catalyst was 1–5 nm. Catalyst particles with sizes of several nanometers were detected on the tips of many of the NT. This provided grounds for proposing a mechanism of the growth, which was called the 'skull-cap' mechanism. According to this mechanism, a catalyst particle promotes dehydrogenation of the hydrocarbon molecules deposited on the particle from the gas phase. Carbon diffuses to the open tip of the NT (where the catalyst particle is located) over the catalyst surface or through the bulk and is embedded in the NT structure. It is the coating

consisting of chemisorbed carbon atoms on the surface of the catalyst particle that is referred to as 'skull-cap'. It prevents the formation of dangling bonds. Micrographs of single-walled NT with catalyst particles located on the open tip and having a size equal to the NT diameter were reported.¹⁶⁸

Testing of the Ni–MgO,^{146,169} Co–MgO¹⁷⁰ and Ni–AlPO₄¹⁶⁹ systems as catalysts for decomposition of CO gave positive results. Not only multi-walled NT¹⁴⁷ but also single-walled NT containing no deposit of amorphous carbon on the external surface have been synthesised from CO.

None of the proposed mechanisms¹⁷¹ is able to explain the influence of the nature of the initial gas on the morphology of NT and other structures.

4. Synthesis of nanotubes containing B–C–N, C–N and B–N

It has been noted above that the catalytic pyrolysis of triazine gives rise to nitrogen-containing NT.¹⁶⁰ The pyrolysis of CH₃CN·BCl₃ at 900–1000 °C over a Co powder afforded fibres and NT of the composition B_xC_yN_z with various morphologies.¹⁷² Nanotubes of the composition C₃₈N, the properties of which differed markedly from those of carbon NT, were obtained from pyridine in the presence of a Co catalyst; the nanotubes BC₂₈N were synthesised from the adduct (CH₃)₃N·BH₃.¹⁷³ All the nanotubes thus prepared were multi-walled. Since the yield of NT in the pyrolysis of the adduct NH₃·BH₃ was very low, it was proposed that coating of metal particles with graphite is a necessary initial stage in the formation of boron- and nitrogen-containing NT.

The data available to date are still inadequate for drawing definite conclusions about the reaction mechanisms, although the shape of some NT provided grounds for speaking about the unusual phenomenon of periodic motion of the catalyst particles located inside the NT along the NT axis.¹⁷² Previously a similar mechanism had been described for purely carbon NT with a bamboo-like structure.¹⁷⁴

VI. Growth of nanotubes by decomposition of metal carbides

When performing arc synthesis, researchers have noticed that particles of catalysts (carbides) are first covered by an envelope of several graphitised layers, which serve as the source for the growth of NT.¹⁷⁵ The mechanism of formation of such a structure (which has been termed 'sea-urchin') includes the formation of super-saturated solutions of carbon in a metal or metal carbide, subsequent segregation of carbon from these solutions and the 'root' growth of NT. 'Sea-urchins' were formed on particles of YC₂,^{71,175} LaC₂,¹⁷⁶ GdC₂,¹⁷⁷ Ni₃C,¹⁷⁸ TiC¹⁷⁹ and other carbides.

Heating of silicon carbonitride under a static atmosphere of N₂ at 1400 °C or in a flow of N₂ at 1850 °C resulted in the synthesis of multi-walled NT with a diameter of 10–25 nm and with a length of up to 1 µm.¹⁸⁰ According to a publication which appeared almost simultaneously,¹⁸¹ laser ablation of α-SiC resulted in sublimation of silicon and the formation of NT on its surface. Soon this process was even more simplified; in particular, laser treatment was replaced by resistivity heating of powdered¹⁸² or single-crystalline¹⁸³ silicon carbide. Heating of powdered silicon carbide *in vacuo* at 1600–1700 °C allowed preparation of NT on a relatively large area over a period of 10–15 min. These NT grew at right angles to the external surface of the powder; they were substantially shorter than those obtained by the arc method but longer than those prepared by the laser ablation of SiC. Even more uniform NT ('a forest') were synthesised at a temperature of 1700 °C and a pressure of 1.3×10^{-2} Pa on a $3 \times 5 \times 0.34$ mm plate. They grew to a length of 0.15 µm over a period of 30 min and were distinguished by a fairly regular mutual orientation. Apparently, this procedure is the simplest way of producing cathodes for field electron emitters.

Small amounts of NT were formed in Fe–Ni and Fe–Ni–Co alloys containing carbon^{184,185} and in complex solid solutions containing Fe₃C.¹⁸⁶ During subsequent studies, this procedure could be modified for the preparation of NT-containing composites possessing specific properties.

VII. Other methods

1. Synthesis in the flame

Combustion of hydrocarbons in oxygen is employed for the synthesis of diamonds (see, for example, Ref. 187) and fullerenes.¹⁸⁸ Nanotubes can also be prepared in this way.¹⁸⁹ It is of interest that the C:O ratios, which were equal to 1.06, 1.07 and 0.86–1.00 for the combustion of C₂H₂, C₂H₄ and C₆H₆, respectively, are close to the optimal values for the synthesis of diamond. However, these processes were carried out under different conditions — in the synthesis of diamond, the inner cone of the flame was directed at a substrate cooled to a particular temperature, whereas in the preparation of NT, catalysts were used.

The data on the synthesis of NT in flames are too scarce to analyse them, as has been done for the synthesis of diamonds (see, for example, Refs 190, 191). It is possible that NT, like diamonds, can be synthesised using any carbon compound, no matter what other chemical elements (halogens, sulfur, nitrogen, phosphorus, silicon, boron, *etc.*) are contained in the compound.

2. Electrolysis of molten salts

Nanotubes can also be synthesised without participation of a gas phase, namely, in ionic salt melts. The electrolysis of molten LiCl at temperatures above 600 °C in a cell with carbon anode and cathode causes a heavy erosion of the cathode and appearance of sludge in the melt, which can be washed by water and toluene after cooling the melt.¹⁹² In addition to spheroidal and polyhedral particles, multi-walled (2–10 walls) NT with a diameter of 2–10 nm were detected in the sludge. The current density has a strong influence on the yield of NT. The yield and the quality of NT also depend substantially on the temperature of the melt and the nature of the salt used (LiCl, NaCl or KCl).¹⁹³ The electrolysis should not be carried out for a long time because the sludge can short circuit the electrodes.

The electrolysis of a LiCl–SnCl₂ melt resulted in the synthesis of NT filled with β-Sn, *i.e.* a nanowire.⁸⁵

3. Chlorination of carbides and other methods

According to a publication,¹⁹⁴ back in the 1960s, multi-walled NT were obtained by chlorination of SiC and TaC at 800–850 °C; the electron micrograph of these NT was published in 1978 in a book.¹⁹⁵ Presumably, the coke that had been prepared using a graphite electric heater (with a temperature of at least 2500 °C) and employed for the synthesis of carbides, served as the source of NT.

There also exist other methods for the synthesis of NT, for example, pyrolysis of the powdered polymer prepared by polyesterification of oxalic acid and ethylene glycol,²⁶ and the reaction of metallic Cs with nanoporous carbon, prepared from a mixture of polyfurfuryl alcohol and polyethylene glycol, carried out at 50 °C.¹⁹⁶

A method for the synthesis of NT similar to that described in Ref. 148, has been proposed by Küttel *et al.*¹⁹⁷ The researchers prepared NT in a microwave discharge using a setup for the plasma synthesis of diamond coatings and a CH₄ (2%)–H₂ (98%) mixture at a pressure of 0.4 kPa; Ni or Fe islets were applied preliminarily on the substrate, the temperature of the substrate being only slightly higher than the optimum temperature for the synthesis of diamonds (900–1000 °C). The deposit had a 'spaghetti' structure and consisted of NT with a diameter of 20–60 nm and a length of up to 100 µm entangled with one another and firmly attached to the substrate. The catalyst particles remained near the NT 'roots' during the synthesis.

The same researchers were able to perform the synthesis of NT using the 'classical' setup used for chemical vapour deposition of diamonds, namely a hot-filament reactor. Since setups similar to that used by Küttel *et al.*¹⁹⁷ are widely employed in dozens of laboratories in many countries and do not need to be modified for switching to the preparation of NT, further development of these methods for the synthesis of NT may be expected.

Recently, syntheses of NT by heating carbon black with boron at 2200 °C and by detonation of 2,4,6-triazidotriazine have been described.¹⁹⁸ An interesting feature of the latter method (explosive synthesis) is that it permits preparation of NT with a record-breaking inner diameter equal to 80–120 nm (although they are formed in a very low yield).

VIII. Purification and opening of nanotubes

Detailed investigation into the properties of NT and some of their practical applications require individual and uniform open-tip NT containing no impurities. However, they are usually obtained as bundles consisting of NT with different lengths, capped at one tip and contaminated with impurities. Therefore, techniques for purification and opening of NT are as important as the methods used to synthesise them.

Unlike fullerenes, neither individual NT nor, all the more so, bundles are soluble in any solvent, which complicates the problem of their purification. Nevertheless, several techniques which permit more or less successful purification of NT have been proposed. The methods are based on the following characteristic features of NT.

The materials that typically contaminate NT (fullerenes, polyhedral graphitised particles, amorphous carbon) are more reactive than NT and some of them (for example, fullerenes) are soluble in organic solvents. Sections of NT with a higher density of defects also exhibit higher reactivity than defect-free NT. This refers first of all to the caps at the NT tips, which contain not only six-membered but also five-membered carbon rings. The carbon atoms in these rings are more reactive. The sections on the lateral surfaces of bent NT possess similar properties because kinks would be impossible without insertion of either five-membered (positive curvature) or seven-membered (negative curvature) carbon rings in a net consisting of standard six-membered rings. Finally, enhanced reactivity is also characteristic of the atoms at the edge dislocations of NT (the 'scroll' or 'papier-mache' structure), in which dangling bonds are concentrated together with defects arising upon replacement of carbon atoms by atoms of other elements.

Multi-walled NT, which are normally more defective than single-walled ones, are more reactive, whereas NT annealed at high temperatures (annealing leads to elimination of defects) are less reactive. Nanotubes filled with metals or metal carbides differ in density from empty NT.

The methods used to purify nanotubes can be divided into three groups — chemical, physicochemical and mechanical.

1. Chemical methods

The simplest method for opening NT is selective oxidation of the caps, which can be carried out by gases, melts or aqueous solutions.

The gaseous oxidants used for this purpose are O₂ (see Ref. 62), air,¹⁹⁹ CO₂ (see Ref. 200) and oxygen plasma.²⁰¹ The maximum rates of oxidation with air are attained at 420 °C for C₆₀, at 645 °C for graphite and at 695 °C for NT or nanoparticles.¹⁹⁹ Oxidation with O₂ or with air proceeds most efficiently at 650–750 °C.

Even at 550 °C, a gas flow containing 1% of O₂ causes disordering of the outer shells of NT and formation of wells with a diameter of 2–10 nm on their surface; as a consequence, thin NT swell up.²⁰² At 750 °C, gasification readily occurs at the sites of cracks, defects or deformations.

After opening of NT, the oxidation slows down, whereas oxidation of nanoparticles goes on until they are completely eliminated.²⁰³ However, complete elimination of nanoparticles requires that more than 99% of the initial material be oxidised. Meanwhile, even after 95% oxidation, a sample contains only 10%–20% of the initial NT. This is due to the fact that not only caps but also lateral walls of the NT are oxidised. As this takes place, multi-walled NT become thinner and some of them are completely gasified.

To purify multi-walled NT in air, heating by IR radiation can be used.²⁰⁴ In particular, a 0.1-mm thick spongy paste with an area of ~10 mm² consisting of multi-walled NT was obtained in this way from the products of arc synthesis in an H₂ flow. In some cases, it is sufficient to heat the material in air at 500–600 °C for 30 min.²⁰⁵

Purification can also be carried out in hydrogen plasma.²⁰¹ However, in practice, purification of multi-walled NT from amorphous carbon is carried out by treatment in an H₂–N₂ mixture at 900 °C.¹³⁷

The method of oxidation in melts^{59,61} has not been further developed.

In the case of single-walled NT, oxidation in aqueous solutions is apparently the most important method. The most frequently encountered procedure is refluxing in concentrated (60%–70%) HNO₃.^{109,203,206–208} The products of catalytic synthesis are freed simultaneously from the inevitable metal impurities. After refluxing for 4.5 h, the loss of mass in the material obtained by the arc method was less than 2%; as a result, 80% of NT became open.²⁰⁶ Refluxing of 10 g of the initial material produced by the laser ablation method in 1 litre of a 2–3 M solution of HNO₃ for 45 h resulted in a 70% loss of weight.¹⁰⁸

Apart from treatment with nitric acid or after this treatment, NT are made to react with mixtures of HNO₃ with H₂SO₄ and of H₂SO₄ with H₂O₂ (see Ref. 103). In some cases, H₃IO₅ and HClO₄ (see Ref. 209) or solutions based on concentrated HCl²¹⁰ have been used instead of HNO₃. Other compounds used as oxidants include H₂O₂, K₂Cr₂O₇, KMnO₄, solutions of Ru and Os chlorides in a solution of NaIO₃, *etc.* Some of the oxidants (acidic solutions of H₂O₂ and K₂Cr₂O₇) proved to be much less selective and efficient than HNO₃, some other (solutions of KMnO₄ containing MnO₂ or CrO₃) exhibited medium activity, and a group of reagents (solutions of Ru and Os chlorides in a solution of NaIO₃) exhibited a very high reactivity and ensured opening of up to 80%–90% of NT at 100 °C.^{211,212}

Oxidation in solutions can be combined with filling of NT (for this purpose, a soluble metal salt is added to the solution^{206,210}) or with chemisorption of metals on the NT surface.²¹³ Chemisorption is due to the fact that upon treatment with an acid, the surface of NT is coated with the acidic groups COOH, which can react with metal ions. The quantity of the Pd²⁺ ions absorbed was found to be strictly correlated with the concentration of acidic groups on closed or open NT.²¹³ An especially high density of acidic groups is attained by using a mixture of H₂SO₄ with HNO₃; these groups promote deposition of finely dispersed metal clusters on the NT surface (see, for example, Ref. 214). The data on wetting, filling and coating of NT have been briefly surveyed in a publication.²¹⁵

Foreign particles can be removed using organic solvents, for example, toluene, carbon disulfide and other solvents, while metal particles can be removed with the aid of acids.

In a pioneering study dealing with purification of NT,²¹⁶ chemical modification of NT by grafting dichlorocarbene to the graphene wall at a double bond has been proposed. In a later publication,²¹⁷ preparation of soluble NT has been reported. The researchers attached a long-chain amide in place of the carboxy groups at the tips of cut single-walled NT. This was attained by treatment of NT with thionyl chloride (70 °C, 24 h) and then with octadecylamine (90–100 °C, 96 h). The product was readily soluble in chloroform, dichloromethane, aromatic compounds

and CS₂. These studies open up new prospects for the development of more facile methods for the purification, separation, study, description and application of NT.²¹⁸

2. Physicochemical and mechanical methods

In recent years, a number of physicochemical and mechanical techniques for the purification of NT have been proposed. They are briefly described below. A physicochemical method, chromatography, has been used to purify both multi-walled²¹⁹ and single-walled NT.²²⁰ The initial NT are dispersed in aqueous media, the dispersions being stabilised by adding surfactants. After separation of the material into fractions using a column with a porous glass packing (with an average diameter of pores of 300 nm), NT are isolated from the individual fractions by centrifuging. Thus not only impurities are removed but, in addition, NT of different lengths are separated.

'Cutting' of NT into 100–300-nm long sections has been reported.²²¹

The foundations of an electrophoretic method for the purification of NT (as a suspension in isopropyl alcohol) have been outlined in a study.²²²

Various mechanical procedures for the purification of NT are known. They include sonication, microfiltration and centrifuging.^{103, 199, 206–208, 223–225} Many of these procedures are labour-consuming and include large numbers of stages; in some cases, they are used only in combination with chemical methods. Sonication increases the density of defects, especially, in multi-walled NT. The ability of individual NT to form bundles ('ropes') manifests itself not only during the synthesis but also in the purification — in some cases, the purified material contains bundles with greater diameters than the initial material. Under some conditions of sonication in acids, the bundles of NT assume a ring shape with a diameter of 0.25–0.55 μm .²²⁶

Particular examples of combined strategies for the purification of single-walled NT can be found in the literature.^{103, 208}

IX. Conclusion

Methods for the synthesis of NT are fewer in number, judging by reviews,^{3, 7} than methods for the synthesis of fullerenes. Nevertheless, the main range of these methods has already taken shape and now the question is what of these methods are best suited for the large-scale synthesis of NT.

Different methods can only be compared conventionally because in most cases, the necessary characteristics are not fully available or not reported at all. First of all, methods that require vacuum or elevated pressures should be distinguished from the procedures of synthesis at ambient pressure. The former are less productive. The vaporisation of graphite induced by electron or ion beams and the use of diamond anvils also imposes some restrictions on the productivity. It is also expedient to classify as a separate group those methods that cannot be easily made continuous, for example, electrolysis or explosive synthesis.

Many investigators agree in the opinion that the most widely used electric-arc and laser-ablation methods are applicable only on a laboratory scale, whereas pyrolysis should become the most important commercial method.^{131, 156, 165, 227} This method is similar in many respects to the pyrolytic method long employed for the production of carbon fibres both in the presence and in the absence of catalysts. The necessary equipment is relatively simple. It is the pyrolytic method that was used to prepare the longest known thread-like bundles of NT and macroscopic ribbons ('mats') of interwoven NT.¹⁶⁵

The advantages of the pyrolytic method are manifested especially clearly in the production of ordered structures by deposition of NT onto a smooth substrate with a supported catalyst or onto a porous template. Neither arc nor laser methods can give such structures. Mechanical expedients have been developed which allow laying of NT of any origin parallel to one another (for example, dispersion in a matrix made of a polymeric

resin followed by cutting thin slices of the composite²²⁸ or microfiltration of a suspension in ethanol through specific ceramic filters followed by transfer onto a plastic surface²²⁹). However, they are all much more complicated and much less elegant than catalytic pyrolysis and cannot in full measure compete with it.

Ordered structures from NT prepared by the pyrolytic method are best suited for template synthesis, *i.e.* application of metals, for example, Ni or Co on their surface,^{142, 230, 231} for deposition of oxides,⁶³ carbides^{232–235} or gallium nitride,²³⁶ for the preparation of catalysts, sorbents, membranes for electrochemical cells,¹⁵² field emitters and artificial muscles (actuators).

Pyrolysis of hydrocarbons in flame¹⁸⁸ and in plasma¹⁹⁶ are also promising because both methods are facile and can be implemented in a continuous mode. Diamond coatings are already prepared on an industrial scale by means of plasma devices; the principal (perhaps, the only) condition for using them for the synthesis of NT is the presence of an appropriate catalyst on the substrate.

However, it may happen that NT meant for particular purposes will be prepared by other methods which have not yet been tested, for example, in plasma jet devices. However, the use of solar energy concentrators for the preparation of NT can hardly be expected in Russia, because the intensity of solar radiation in Russia is relatively low and the level of development of this method does not surpass that for other methods of heating.²³⁷

Studies of carbon NT have provoked interest in the preparation of nanotubes consisting of other inorganic compounds. Tubular structures are possible for a fairly large number of inorganic compounds of various classes.²³⁸ Studies on the synthesis of NT from BC_x, BN, BC_xN_y and CN_x are only at the beginning; however, in this case, too, pyrolytic methods would apparently prove to be the most convenient.

The problem of the synthesis of NT with identical geometries might be solved using the method proposed by Smalley, namely, selection of homogeneous seed NT and their further growth by pyrolysis of hydrocarbons (<http://www.dtic.mil/dusdst/agenda/agenda31999.html>).

A complicated synthetic task would be routine preparation of NT with reproducible heterojunctions (variation of diameter, chirality or chemical composition); some enthusiasts believe that this could serve as the basis for the nascent nanoelectronics. The design of nanomechanical devices in which NT are expected to serve as important and abundant parts will also require great efforts.

* * *

Since this manuscript was prepared for the publication, new journal papers and Internet sites devoted to the synthesis of carbon NT have appeared (or become available).

Thus the mechanism of formation of carbon NT, nanowires and nanoparticles in an electric arc burning under a hydrogen atmosphere has been described. The participation of polycyclic aromatic hydrocarbons in the synthesis of NT has been confirmed. A direct correlation between the ability of H₂ to remove graphenes from an anode and the yield of NT has been elucidated.²³⁹

It was found that only three platinum metals, Rh, Pd and Pt, induce the formation of single-walled NT in an electric arc, whereas mixtures of metals (Ru–Pd, Rh–Pd, Ru–Rh, Ru–Pt and Pd–Pt) exhibit low or zero activity; only a Rh–Pt mixture (1 : 1 or 5 : 2) is active in this process.²⁴⁰ At a helium pressure of 78 kPa over a Rh–Pt catalyst, NT with approximately equal diameters (1.28 $\pm$ 0.07 nm) were formed. A 10–12 fold decrease in the helium pressure resulted in the growth of nanotubes of different diameters (0.7–1.3 nm).

A novel method for the synthesis of NT in a pulsed arc setup has been developed.²⁴¹ The highest yield of NT was attained in a

flow of Ar or Kr at temperatures of $> 1000\text{ }^{\circ}\text{C}$ and pulse duration of $> 1\text{ }\mu\text{s}$.

Interesting results concerning growing of NT by the electric-arc method have been obtained in a study by Chang *et al.*,²⁴² who used an anode with a diameter of 6 mm and a 10-mm thick disk 30 mm in diameter as a cathode. Both electrodes were intensely cooled with water and the electrolysis was carried out in a self-sustained mode (interelectrode distance 3–4 mm, voltage 20 V, current 55–65 A, helium pressure 67 kPa). The cathode deposit was formed on an area with a diameter close to the anode diameter. The morphology of the deposit differed appreciably from the standard morphology. A bed of chaotically entangled slightly bent NT (diameter 10–40 nm, length $> 30\text{ }\mu\text{m}$), the axes of which were oriented randomly, was located under a thin tough shell. These NT had no defects, contained no amorphous carbon impurity and could be purified from the nanoparticle impurity by merely keeping in air (850 $^{\circ}\text{C}$, 1 h). The intense cooling of the electrodes and gases near the cathode as well as the large distance between the electrodes, which influences the mode of the current passage, is assumed to be largely responsible for the sharp change in the morphology and properties of the arc synthesis products.

A detailed study of some parameters of the laser-induced thermal synthesis of NT has been reported.^{243,244} In particular, it was found that the amount of carbon being vaporised from the target is determined by the intensity of laser radiation, while the course of the chemical reaction yielding NT is governed by the temperature in the furnace. The rate of evaporation of catalysts (Ni and Co) is affected by both parameters. The laser radiation intensity has a slight influence on the diameter of NT, while a decrease in the furnace temperature results in smaller diameters.²⁴³ The increase in the delay between single laser pulses from 0.1 to 120 s has almost no influence on the structure of single-walled NT but decreases the yield of the web-like product.²⁴⁴ It has been shown theoretically²⁴⁵ that the use of shorter pulses (picoseconds instead of nanoseconds) and higher frequencies (tens of megahertz) brings the synthesis of NT closer to a quasi-continuous mode.

It has been shown²⁴⁶ that the laser-assisted synthesis of NT in the presence of Ni and Co can also be performed in a flow of N_2 .

The application of a continuous-wave CO_2 laser to the synthesis of NT without additional furnace heating of the target is a method new in principle.²⁴⁷ In this study, a vertical setup was used with a rotating target moving along its axis (a rod 6 mm in diameter) and made of a mixture of graphite with a catalyst. A hot zone with a diameter of $\sim 1\text{ cm}$ was formed around the laser spot; this resulted in local heating of the gas flow and prevented the plasma from cooling too fast. The synthesis was carried out under Ar. When the radiation power was 250 W and the diameter of the laser spot was $\sim 1\text{ mm}$, the vaporisation rate reached 200 mg h^{-1} . The yield of single-walled NT in the presence of Ni–Y or Ni–Co catalysts was $\sim 20\%$ based on the amount of the vaporised material.

French investigators have successfully tested a prototype of a 1000-kW solar concentrator for the synthesis of NT (<http://www.uiuc.edu/cnrs/Cnrspresse/en352a3.htm>).

The formation of NT on irradiation of graphite with high-energy Ne^+ , Kr^+ and Xe^+ ions has been studied.²⁴⁸

Numerous publications in 1998–1999 were devoted to the pyrolytic synthesis of NT. For instance, the influence of the substrate on the catalytic pyrolysis of C_2H_2 in the presence of Co or Fe has been considered.²⁴⁹ The influence of the natures of the catalyst (Fe_2O_3 , CoO , NiO or their mixtures) and the support (Al_2O_3 or SiO_2 with a specific surface area of 100 and $300\text{ m}^2\text{ g}^{-1}$, respectively) on the formation of single-walled NT in the pyrolysis of pure CH_4 has been studied.²⁵⁰ Relying on the fact that the tips of growing NT contained no catalyst particles, the researchers²⁵⁰ concluded that the process followed a ‘root’ growth mechanism. The highest yield of individual NT was attained with the $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst.

The pyrolysis of metallocenes and $\text{Fe}(\text{CO})_5$ mixed with C_2H_2 or C_6H_6 has been studied.^{251,252} It was found that the content of the amorphous carbon impurity can be diminished by introducing H_2 into the gas phase.

The conduct of the pyrolysis of C_2H_2 by means of a hot filament with plasma activation permitted the substrate temperature to be decreased to $650\text{ }^{\circ}\text{C}$.^{253,254} Yet another novelty was the use of an NH_3 admixture, which was found to function as a catalyst. The diameter of the NT produced in this way was dictated by the thickness of the Ni film sprayed preliminarily onto a glass substrate and varied from 20 to 100 nm. The growth rate was several times higher than that attained in earlier studies (see, for example, Ref. 133) and was equal to $120\text{ }\mu\text{m h}^{-1}$.

Pyrolysis of naphthalene vapour in the presence of $\text{Cr}(\text{CO})_6$ vapour with ‘anode field activation’ was performed for the first time.²⁵⁵ The process at a voltage of 4–6 kV, an anode temperature of 1100–1200 $^{\circ}\text{C}$ and a vapour pressure of $\sim 8\text{ Pa}$ afforded carbon NT with Cr nano-rods protruding from their inner cavity. These rods had a strictly invariant diameter ($\sim 10\text{ nm}$) along the full length (up to $0.5\text{ }\mu\text{m}$). The attempts to accomplish a similar process with $\text{Mo}(\text{CO})_6$ or $\text{W}(\text{CO})_6$ failed.

Yet another modification of the pyrolytic synthesis of NT includes two-stage heating *in vacuo* (first at 350–450 $^{\circ}\text{C}$ and then at 500–800 $^{\circ}\text{C}$) of tripropylamine introduced in the channels of $\text{AlPO}_4\cdot 5$ single crystals.²⁵⁶ The NT thus formed had equal diameters and equal lengths; however, they proved to be unstable with respect to HCl.

Nanotubes consisting of a new promising material, carbon nitride, have been prepared on a graphite substrate from a $\text{C}_2\text{H}_2\text{--N}_2$ mixture in a microwave plasma using a bias potential.²⁵⁷ A peculiar method for the synthesis of B,N-containing NT is based on the replacement of C atoms in carbon NT by B and N atoms upon the reaction of NT with B_2O_3 vapour diluted with N_2 .²⁵⁸ The preparation of multi-walled NT filled with molten UCl_4 or its mixtures with KCl has been described.²⁵⁹

A method for purification of NT (prepared by the pyrolysis of C_2H_2 over Co introduced into NaY zeolite) has been described, which involves dissolution of impurities in hydrofluoric acid and subsequent oxidation of NT with a solution of KMnO_4 or air.²⁶⁰

A fairly comprehensive study²⁶¹ is devoted to the behaviour of NT treated with a mixture of concentrated HNO_3 and H_2SO_4 . The presence of acid functional groups on the surface of these NT makes it possible to prepare viscoelastic gels; on drying, solid materials or films with specific structures and properties can be obtained. Under particular conditions, the dispersions can be converted into a material reminiscent of liquid crystals.

Fullerenes have been synthesised by irradiation of $\text{C}_6\text{H}_6\text{--O}_2$ or $\text{C}_6\text{H}_6\text{--N}_2\text{O}$ mixtures with a CO_2 laser in the presence of SF_6 .²⁶² This method might also enable the synthesis of NT.

The preparation of Langmuir–Blodgett films from matrix-diluted single-walled NT and application of the films onto various surfaces using micelle-like aggregates has been reported.²⁶³ Soluble carbon NT coated with poly(phenylacetylene) have been synthesised.²⁶⁴

Many of the studies mentioned above were reported at the conference on commercialisation of the achievements in the large-scale production of carbon NT (USA, Washington, April 1999; <http://www.knowledgefoundation.com/carbon.html>). The prospects for the investigation and use of NT-based materials were also discussed at the conference of the Materials Research Society (USA, Boston, December 1998), which has been described in a brief review.¹⁹⁷

Studies on the application of NT in electronics were surveyed by Johnson at the International Conference on Solid-State Circuits (USA, San-Francisco, January 1999; <http://www.eet.com/story/OEG19990217S0045>).

Several new promising fields of application of NT have appeared quite recently. The greatest interest was aroused by the development of a prototype of artificial muscles, actuators, activated by application of a low electric potential, which was

reported by an international group of scientists^{265–268} (see also M Fox *Infoseek News* May 21, 1999; http://www.mpg.de/news99/news26_99.html; and <http://www.msnpc.com/news/271534.asp>). A new route to the design of NT-based parts of electronic devices (amplifiers, switches, logical elements) was discovered.²⁶⁹ The possibility of isotope separation with the aid of NT²⁷⁰ and of using NT for nanolithography²⁷¹ was demonstrated. An electrode manufactured from a single NT was developed and tested.^{272, 273}

Recent reviews and issues of journals devoted to NT are also worth mentioning.^{274–282}

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Hybrid polymer-inorganic nanocomposites

A D Pomogailo

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Abstract. Approaches to the preparation of organic–inorganic nanocomposites are considered from a unified viewpoint for the first time. The major problems in the development of this new line of research in materials technology, which has arisen on the border of the science of polymers, colloid chemistry and physical chemistry of the ultradisperse state, are discussed. The main methods for the formation of composite materials and polymer–inorganic cross-linked hybrids with interpenetrating networks are analysed. Primary attention is given to sol-gel procedures for their preparation, including template processes, which occur under conditions of strict stereochemical orientation of reactants, intercalation of monomers and polymers into porous and layered matrices and their intracrystalline and post-intercalation transformations. Methods for the synthesis and properties of metallopolymeric polymolecular Langmuir–Blodgett films, which are peculiar supramolecular ensembles incorporating nanosized metal-containing particles, are discussed. The generality of the processes of formation of organic–inorganic nanocomposites in living and nonliving natural objects is demonstrated and the major fields of application of nanocomposites are considered. The bibliography includes 566 references.

I. Introduction

The science dealing with nanocomposites, which belong to the class of composite materials characterised by nanometer sizes of their structural elements (particles of metals, metalloids, their oxides, chalcogenides, *etc.*), has arisen in recent years on the border of different areas of knowledge. Apparently, the term ‘nanocomposites’ was proposed for the first time by Theng in 1970.¹ In the literature, the terms ‘hybrid nanocomposites,’ ‘nanohybrids’ and ‘nanostructural composites’ are generally used and the terms ‘metallomatrix composites,’ ‘monophase hybrids,’ *etc.* are more rarely used for describing materials

consisting of an organic phase (polymer) and a nanodispersed mineral phase. If a polymer of biological origin serves as a component or a precursor of these polymer–inorganic materials, the term ‘nanobiocomposites’ is used.

An organic phase can capture metal-containing particles into a ‘trap’ of a peculiar kind, *viz.*, into an oxopolymeric network or a polymeric unit with appropriate parameters. Silicon, aluminium, titanium, zirconium, vanadium and molybdenum oxides, glasses, clays, layered silicates and zeolites, metal phosphates and chalcogenides, iron oxychloride and graphite are used as inorganic precursors. Zeolites (molecular sieves) are of particular interest since methods for control over their pore sizes are well known. Not only carbon-chain but also organoelement (generally, organosilicon) polymers are used as a polymeric component. In the resulting nanocomposite materials, distances between networks and layers formed by polymeric and inorganic ingredients and sizes of particles formed, including metal-containing particles, are nanometric.^{2,3}

Generally, hybrid nanocomposites exhibit a synergism of the properties of the initial components. These compounds are characterised by an enhanced mechanical strength and thermal stability and provide optimum heat transfer.^{4,5} In metallomatrix composites, the strength and hardness of soft metals, for example, of aluminium, are enhanced. These materials possess good thermochemical, rheological, electrical and optical properties.^{6–8} These compounds are used as chromatographic carriers, membrane materials,⁹ optical and magnetic materials, components of polymeric compositions, carriers and catalysts of various reactions (see Section VIII).

Currently, numerous procedures for the preparation of nanocomposite materials are available. Recently, the major synthetic approaches (evaporation of elemental metal with its deposition on polymeric matrices, plasma-induced polymerisation, vacuum evaporation of metals, thermal decompositions of precursors in the presence of polymers and reduction of metal ions using different procedures, including electrochemical, *etc.*) have been surveyed in reviews.^{2,3} However, the uniform distribution of ingredients is generally difficult to achieve when hybrid nanocomposites are prepared with the use of the above-mentioned procedures resulting in the nonuniformity of the properties of the material. The following three principal procedures are most commonly employed: (1) the sol-gel method; (2) intercalation of polymers and nanoparticles into layered structures (including

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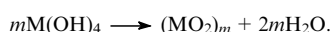
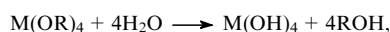
polymerisation *in situ*) with the use of approaches applied in the chemistry of intracrystalline structures ('guest–host' systems); (3) a combination of polymerisation and formation of nanosized particles, which provides homogeneous dispersion of an inorganic component (which is often a specific filler) in a polymeric matrix.

In the last decade, these procedures, particularly, the first and second methods, have received primary attention. The properties and procedures for the synthesis of metallopolymeric Langmuir–Blodgett films are being extensively studied. The results of investigations in this field are summarised in a number of monographs and reviews^{10–34} as well as in special issues of journals.^{35–37} Note that nanocomposites containing not only synthetic but also natural molecules, including biologically active macromolecules, can be conveniently prepared using the above procedures. These procedures have been used for constructing biosensors, enzyme electrodes and other materials based on enzymes. These materials have already found use in biochemistry, medicine, biotechnology and the technology of environmental control.

In the present review, procedures for the preparation of hybrid organic–inorganic nanocomposites are considered from a unified viewpoint and the generality of the processes of their formation in living and nonliving natural objects is demonstrated. Thanks to the help of colleagues from different countries who responded to my requests and sent copies of their latest articles, the review surveys fresh results and the data under consideration were generally published within the last decade.

II. Preparation of hybrid nanocomposites by the sol-gel method

From the ecological viewpoint, optimum procedures for the preparation of composite materials are those without outflow, in particular, the sol-gel method (sol-gel or spin-on-glass process). The latter method allows one to exclude numerous stages of washing because compounds, which are used as the initial compounds, do not contaminate the final product. The sol-gel method is a convenient procedure for the preparation of dispersed materials, which are often called ceramers. This method is based on polymerisation reactions of inorganic compounds (formation of metalloxo polymers in solutions) and involves the following stages: (1) preparation of a solution, (2) formation of a gel, (3) drying and (4) thermal treatment. It is common practice to use metal alkoxides $M(OR)_n$ ($M = \text{Si, Ti, Zr, VO, Zn, Al, Sn, Ce, Mo, W, lanthanides, etc.}$; $R = \text{Alk or Ar}$), which are hydrolysed upon addition of water, as the starting compounds. The reactions are carried out in organic solvents. Subsequent polymerisation (condensation) affords a gel. For example, when $n = 4$



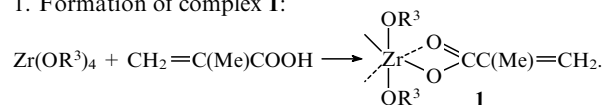
This method is sometimes called 'a one-stage procedure' because both reactions, *viz.*, hydrolysis and condensation, are catalysed by the same compound (by acid, base or, sometimes, by a nucleophilic catalyst, such as NaF).^{14, 38} These reactions with the participation of $Si(OR)_4$ have long been known. Apparently, the preparation of monodisperse TiO_2 particles by hydrolysis of alkoxides has been described for the first time by Barringer and Bowen.^{39, 40}

It is needless to say that the real process is much more complicated and occurs according to a multiple-route mechanism. Generally, metal oxoalkoxides $MO_n(OR)_m$, including polynuclear compounds, are formed as intermediates. Thus hydrolysis of $Ti(OR)_4$ proceeds in two stages,^{27, 41} *viz.*, nucleophilic replacement of the alkoxy group by the hydroxy group and condensation in the course of which oxo and hydroxo bridges are formed. It was demonstrated that the rates of these reactions are comparable.⁴² The $Ti_xO_y(OR)_{4x-2y}$ compounds were isolated and characterised.⁴³ Generally, the controlled synthesis of hybrid nanocompo-

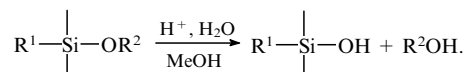
sites based on zirconium alkoxysilanes and alkoxides proceeds according to Scheme 1.

Scheme 1

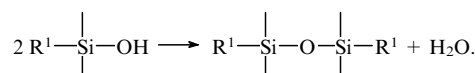
1. Formation of complex **1**:



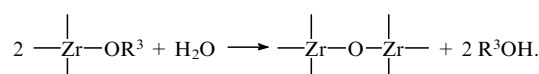
2. Hydrolysis:



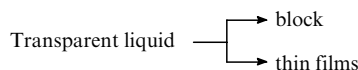
3. Condensation to form latent water:



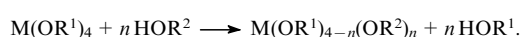
4. Addition of complex **1** and removal of free and latent water by condensation:



5. Addition of a photoinitiator:



The following reaction conditions are of great importance: the use of catalysts, including polymeric catalysts (for example, polystyrenesulfonic acid⁴⁴); the nature of the alkoxy group and of metal [for example, $Ti(OBu)_4$ is hydrolysed almost 150 times more slowly than $Ti(OEt)_4$ (see Ref. 45)]; the use of alkoxides of a mixed type, particularly, with chelate ligands (β -diketonate, α - or β -hydroxy acid, polyol, *etc.*); the degree of association of alkoxides {for example, in the case of $[Ti(OEt)_4]_m$ $m = 2$ or 3}; the formation of oxo or alkoxo cluster structures [for example, $Ti_{18}O_{22}(OBu)_{26}(acac)_2$] in the course of hydrolysis. The reactivity of alkoxides $M^{IV}(OR)_4$ increases in the series $Si \ll Sn$ and $Ti < Zr < Ce$.⁴⁶ The ionic radius of the M atom (0.04 and 0.06 nm; and 0.064, 0.087 and 0.102 nm, respectively), its coordination number (4 and 6; and 6, 7 and 8, respectively) and the degree of its nonsaturation (the difference between the coordination number and the valence; 0 and 2; and 2, 3 and 4, respectively) increase in the same order.⁴⁷ However, the $H_2O : M(OR)_4$ ratio (γ) is of prime importance. Thus in the case of $VO(OPr^i)_3$, a homogeneous transparent gel with an alkoxide polymer network is formed in *n*-propanol if $\gamma = 3$, whereas if $\gamma > 100$, the resulting gel attains a quite different structure, which prevents the formation of an inclusion compound. Besides, the formation of a gel is affected by the nature of the medium, the concentration of the initial solution of an alkoxide, the presence of a stabiliser and the reaction temperature.^{48–50} The thermal effects of hydrolysis of $Ti(OR)_4$ in ROH increase when $\gamma = 0.2–1$, whereupon they remain virtually unchanged. This corresponds to the thermal effect of replacement of one alkoxy group by the hydroxy group.⁵¹ The solid phase with composition $TiO_x(OBu)_{4-2x} \cdot yBuOH$ was obtained upon hydrolysis of $Ti(OBu)_4$ in butyl alcohol through intermediate formation of $TiO(OBu)_2$.^{45, 51} The x and y values increase as the concentration of titanium alkoxide in a solution increases. Unfortunately, the effect of the nature of the solvent (generally, alcohols) on these processes has received little attention in experimental studies. It is known that hydroxy-containing compounds (for example, AlkOH, HOH or R_3SiOH) can take an active part in transesterification in the systems



The nature of metal and the ligand in alkoxides affects substantially these reactions.^{52–54} Thus $\text{Ti}(\text{OPr}^i)_4$ and $\text{OV}(\text{OPr}^i)_3$, which are often used as cocondensates in the preparation of nanocomposites by the sol-gel method,⁵⁵ act as catalysts in transesterification of tetramethoxy- and tetraethoxysilanes (TMOS and TEOS, respectively).

Therefore, the sol-gel process involves hydrolysis, polymerisation (chemically controlled condensation) of a gel precursor, nucleation and growth of particles followed by their agglomeration.^{56,57} TMOS and TEOS are most often used as precursors. They form silica gel structures ('host') about a dopant ('guest'), thus creating a specific cage trap. Nucleation proceeds through formation of a polynuclear complex. Its concentration increases until slight supersaturation, which is determined by the solubility of the complex, is achieved. From this time on, new nuclei do not form and only the available nuclei grow. To put it differently, these processes are analogous to the processes of formation of nanosized particles in polymers.² In the stage of formation of a gel (gelatination), it can be impregnated with ions of different metals.

The resulting oxopolymers have structures of ultrathin porous networks with pore sizes of 1–10 nm similar to the structures of zeolites. Their specific surface (S_{spec}) varies in the range of 130–1260 $\text{m}^2 \text{g}^{-1}$ depending on the conditions of the synthesis, and the bulk density is 0.05–0.10 g cm^{-3} . Thus molecular sieves based on silicon oxides, which are characterised by different mesopore structures and S_{spec} of $\sim 1000 \text{m}^2 \text{g}^{-1}$, were prepared by the sol-gel method in the presence of surfactants.^{58,59} The specific surface of the powder prepared by hydrolysis of $\text{Ti}(\text{OEt})_4$ was 200–300 $\text{m}^2 \text{g}^{-1}$; S_{spec} of hydrolysis products of $\text{Ti}(\text{OBu})_4$ strongly depends on the concentration of the initial solution of alkoxide and attains 490 $\text{m}^2 \text{g}^{-1}$ at the concentration of 1.0 mol litre⁻¹.⁴⁵ Concentrated aggregatively stable hydrosols (containing up to 40 mass % of TiO_2) can be prepared⁶⁰ by secondary dispersion of xerogels formed after drying of the sol (the TiO_2 content is ~ 85 mass %) at 100 °C for 2 h. The sol contains crystalline TiO_2 particles of an average size ~ 3 nm. These particles are a mixture of two polymorphic modifications of TiO_2 , *viz.*, rutile and anatase, with the latter slightly predominating. The third modification (brookite) is formed much more rarely. In these systems, single crystals of the anatase phase are often metastable. Compounds containing labile vinyl, methacrylate, epoxy and other groups can act as cross-linking agents (see Scheme 1). The conditions of drying in the course of which volatile components are removed determine the texture of the product. Thus coarse-dispersion xerogels can form upon prolonged drying in air due to coalescence of gel particles. Under conditions precluding the action of capillary forces, highly dispersed aerogels are formed. The formation of the structure and texture of the product is completed in the stage of thermal treatment.^{10, 61–65}

The sol-gel method with the use of highly dispersed silica gel in a polar solvent is applied in microencapsulation of photochromic fluorescent compounds,⁶⁶ scintillators¹⁷ and porphyrins. A sol-gel matrix for encapsulation is prepared by simultaneous hydrolysis of $\text{Si}(\text{OEt})_4$ – $\text{Zr}(\text{OBu})_4$ and other alkoxides.^{67–69} Thermally stable materials, which are used in nonlinear optics, can be prepared by introducing, for example, azo dyes into TMOS by the sol-gel method.⁷⁰ Although these systems (except for biologically active systems; see Section IV) are not considered in this review, they are structurally similar to nanocomposites and are prepared according to analogous procedures. Thus the introduction of methyl methacrylate (MMA), in which an organic dye of the perylene type was dissolved, into a xerogel followed by thermal or UV polymerisation, afforded a coimpregnated SiO_2 –poly-methyl methacrylate–dye system.^{71,72} The technique for sublimation dehydration of impregnated gels was developed.⁷³ This technique allows one to prevent redistribution of labile components in the matrix in the course of drying.

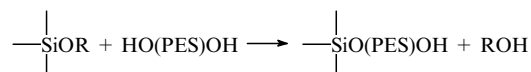
Sol-gel materials are classified by a mode of formation and types of bonds between organic, organometallic and inorganic

components.¹⁷ Organic groups introduced into $\text{R}_n\text{Si}(\text{OR}^2)_{4-n}$ serve two functions,^{74,75} *viz.*, modify a network (ORMOSIL, organically modified silicates) and form a network (ORMOCER, organically modified ceramics). However, this classification has not yet received ample recognition. Low-percentage and high-percentage composites contain 2 vol. %–30 vol. % and up to 45 vol. %–75 vol. % of ceramics, respectively. Thus a material under the name 'rubber ormosil' (based on TEOS and polydimethylsiloxane with $M_w = 1700$) contains more than 70 vol. % of an inorganic component.^{76,77}

Hybrid nanocomposites are primarily classified by the type of interphase interactions between components. Thus nanocomposites whose macrostructures are determined by the presence of van der Waals, hydrogen or hydrophilic–hydrophobic interactions are known. These are, for example, amorphous inorganic nanocomposites, which are prepared from silicon-, titanium-, aluminium- or zirconium-containing oxopolymers formed *in situ* in a medium of a soluble organic polymer. Formally, this process consists in homogeneous formation of a nanosized filler in a medium of a polymer. Poly(*n*-butyl acrylate), polyphosphazene, polyvinylpyrrolidone (PVP), poly(*N,N*-dimethylacrylamide), *etc.* were prepared according to this procedure.^{78–82} An alternative procedure involves the insertion of a polymer (or its precursor) into an oxogel, which is formed by mixing of metal alkoxides or by their impregnation into pores of an oxide xerogel network. Either organic molecules or polymers are inserted as 'guests' into nanocomposites of another type.

The one-stage formation of oxogels and polymers is exemplified by sol-gel polymerisation (including electrochemical polymerisation) of the so-called silanised monomers, *viz.*, *N*-[3-(trimethoxysilyl)propyl]pyrrole,^{83,84} 2,5-bis(trimethoxysilyl)thiophene⁸⁵ and trimethoxysilylferrocene derivatives.⁸⁶

Hybrid network composites in which organic and inorganic components are linked through strong covalent or ionic bonds have received primary attention. These networks are generally prepared according to two procedures: (1) secondary networks are formed in primary networks, which are functionalised as required; (2) two different networks (including interpenetrating networks) are simultaneously formed from molecular precursors of a different nature, which enter into different reactions (polyaddition, polycondensation, metathesis polymerisation, hydrolysis–condensation, *etc.*). This line of investigation is in a primitive state of development and reliable examples of realisation of this approach are few in number.^{87–89} Initially, it was attempted to use solutions of polymers. However, the formation of a gel was accompanied by uncontrolled phase separation to yield a heterogeneous material. More homogeneous sol-gel materials were prepared⁹⁰ by acid-catalysed hydrolysis simultaneously with condensation of $\text{HO}(\text{PES})\text{OH}$ [PES is (polyethersulfone)] and TEOS or TMOS in DMF.



Inorganic and polymeric components are linked *via* deep interactions. Thus poly(ethersulfone) chains are linked through $\text{—SiO}_2\text{—}$ units. Their condensation affords nanoparticles (Fig. 1).⁹¹

Bonding of TEOS, diethoxydimethylsilane or their mixture with sulfo groups of perfluoroalkylsulfonate ionomers (under the commercial name Nafion) in which the SO_3H^+ groups form clusters with sizes 3–5 nm affords a hybrid heterogeneous material Nafion/ SiO_2 (Nafion/ORMOSIL).^{92–96} Studies by differential scanning calorimetry demonstrated that a broad endothermic peak of the initial NafionH^+ at 215 °C was shifted to the lower-temperature region as the ratio of the components of the reaction mixture was changed. This is associated with condensation between the sulfo groups of Nafion and the silanol groups. In the course of the sol-gel process with the participation of TEOS and the styrene–maleic anhydride copolymer in the presence of a

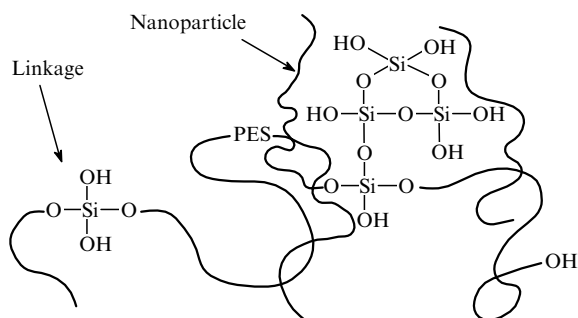
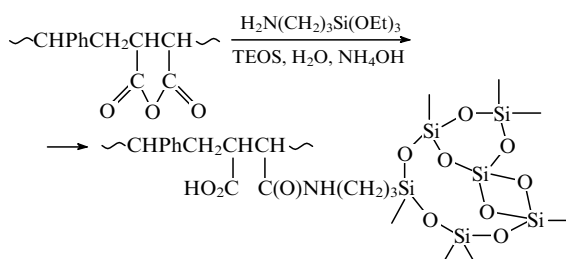


Figure 1. Formation of a hybrid nanocomposite in the reaction of PES with bridging $-\text{SiO}_2-$ groups.

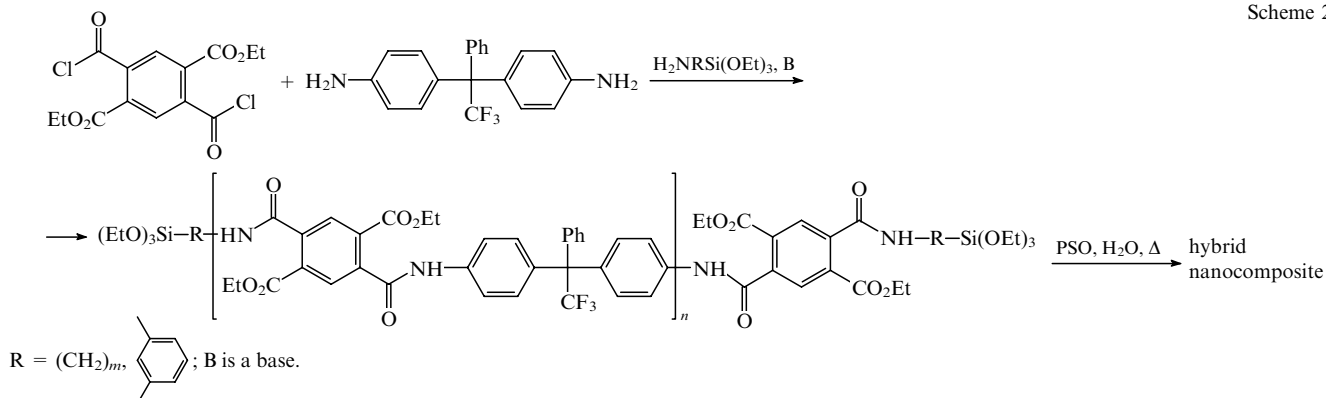
binding agent, *viz.*, (3-aminopropyl)triethoxysilane, a covalent bond between polymeric and inorganic components was also formed.⁹⁷ In this case, particles with sizes < 20 nm were formed.



A series of monolithic hybrid materials containing 23 vol. %–100 vol. % of an inorganic component were prepared by the sol-gel method starting from SiO_2 and the copolymer of methyl methacrylate with 3-(trimethoxysilyl)propyl methacrylate.^{98,99}

Polyimide composite materials containing nanosized SiO_2 or TiO_2 particles possess the high mechanical strength due to their ability to form three-dimensional inorganic networks.^{100,101} Polyimide–polysilsesquioxane[†] composites were prepared, for example, by condensation of 1,1-bis(4-aminophenyl)-2,2,2-trifluoro-1-phenylethane with a derivative of pyromellitic anhydride and aminophenyltrimethoxysilane (simultaneously with imidisation at 250 – 350 °C).^{104–107} In this case, films of hybrid nanocomposites containing 32%–70% of homogeneously dis-

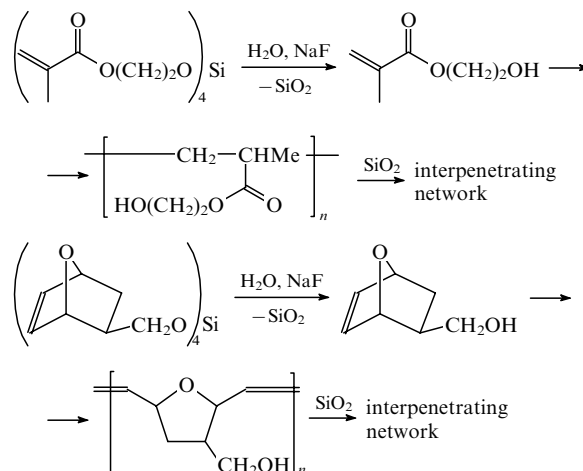
[†]Polysilsesquioxanes (PSO) belong to a class of three-dimensional organosilicon oligomers of the general formula $(\text{RSiO}_{1.5})_n$ containing the inorganic cubic Si_3O_{12} nucleus. These compounds have polyhedral structures with different symmetries and are key intermediates in the formation of various nanocomposites (see, for example, Ref. 102). Thus the synthesis and properties of hyperelastic materials, which have been prepared by copolymerisation of 4-methylstyrene and oligomeric silsesquioxane macromers, have been reported recently.¹⁰³



persed SiO_2 with particle sizes of 0.5 – 7 nm were obtained (Scheme 2). Polyamide– SiO_2 compositions were prepared *in situ* by suspending SiO_2 nanoparticles (which were sometimes preliminarily modified with aminobutyric acid) in a polymerised ϵ -caproamide at high temperature.^{108,109} This approach provides homogeneous distribution of SiO_2 owing to which the mechanical properties of nanocomposites are improved, the glass transition temperature rises and the rate of crystallisation is increased.

Analogous nanocomposites were also prepared¹⁷ based on analogues of polyimides, *viz.*, polyoxazolines, including those containing triethoxysilane groups.^{110–112}

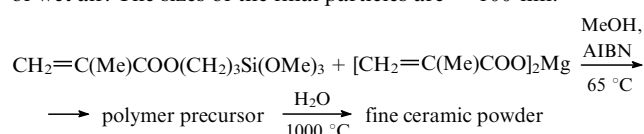
Metathesis polymerisation accompanied by opening of the ring and free-radical addition of cyclic alcohols appears to be the optimum procedure for the synthesis of hybrid SiO_2 –polymer nanocomposites exhibiting the minimum shrinkage.^{31,113–115} The synchronous formation of interpenetrating networks occurs as a result of competitive reactions of polymerisation and hydrolysis of silicon alkoxide under the action of the nucleophilic catalyst NaF followed by condensation.



It is known that sols are thermodynamically unstable systems with high surface free energies. It is necessary to stabilise these systems by special techniques, for example, by controlling pH of the system. When the sol-gel method is used, nanosized particles or their precursors are stabilised through adsorption of special monomeric molecules on the sol surface.^{116–119} Thus carboxylic acids (including polymeric acids^{106,120}) are strongly bound to the surface of SiO_2 , ZrO_2 , TiO_2 or Al_2O_3 particles. Amines are specifically adsorbed on metallic Pd or Au particles. Thiols are even more specific reagents for Au. Controlled hydrolysis with the use of bifunctional molecules containing a double bond along with hydrolysed silane or ZrOR groups affords the corresponding precursors (see Scheme 1). These precursors incorporate ZrO_2 particles of size ~ 2 nm, which can undergo copolymerisation, for example, with methacrylic acid (MAA). The latter simultaneously acts as a surface modifier due to the presence of a double bond.

Scheme 2

Alkoxide Zr(OR)_4 is readily hydrolysed. Direct hydrolysis of the latter affords a precipitate of $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$, which is unsuitable for the preparation of a homogeneous composite material. In strongly acidic media, a flocculent hydrated gel layer is present on the surface of these particles. This layer contributes significantly to the stability towards aggregation.¹²¹ It is believed¹²² that this layer makes it possible to perform repeated peptisation of ZrO_2 from a xerogel. When bound to MAA, Zr(OR)_4 is hydrolysed more slowly and hence well-dispersed nanosized ZrO_2 particles are formed in the presence of latent water. Silanes modified with MAA undergo copolymerisation. In this case, the resulting silicon-containing polymer is used as a matrix material for nanosized zirconium particles (Fig. 2).⁷⁶ A convenient procedure for the synthesis of these nanocomposites involves dispersion copolymerisation of monomers containing trialkoxysilyl groups.^{123–127} Thus statistical copolymerisation of silicon–magnesium monomers affords beads of sizes 100–500 nm from which organic compounds are removed upon heating to 1000 °C in the presence of wet air. The sizes of the final particles are ~ 100 nm.¹²⁸



AIBN is an initiator [2,2'-azobis(isobutyronitrile)].

A nanocomposite material was prepared starting from methacryloxypropyltrimethoxysilane.⁷⁶ The reaction of equimolar amounts of Zr(OR)_4 and MAA yielded a product, which was mixed with silane. The latter was preliminarily hydrolysed and condensed in the presence of 0.5 M HCl, and then H_2O was added. A photoinitiator and alcohol were introduced into the resulting mixture to control the viscosity and then a support was submerged in the mixture thus depositing a thin film of a photosensitive material.

Hybrid nanocomposite materials are prepared from metal-containing monomers, such as alkoxy derivatives of Ti and V of the general formula $\text{Ti(OR}^1)_3(\text{OR}^2)$ ¹²⁹ or $\text{OV(OR}^1)_3\text{--}_n(\text{OR}^2)_n$,¹³⁰ respectively, where R^2OH is ethylene glycol monomethacrylate, 2-hydroxyethyl methacrylate, furfuryl alcohol, 1,1-dimethylpent-4-en-2-yn-1-ol, propargyl alcohol or other unsaturated alcohols,

which are able to undergo polymerisation. Radical polymerisation of metal-containing monomers affords polymers with side chains containing alkoxy groups of titanium¹³¹ or vanadium.¹³² The reactions of MAA with alkoxy derivatives of titanium yield metal-containing monomers $[\text{CH}_2=\text{C}(\text{Me})\text{COO}]\cdot\text{Ti(OR)}_3$ ($\text{R} = \text{Et, CH}_2\text{Bu}^t$ or Bu^t).¹³³ Based on these compounds, nontoxic, self-polished and anticontamination coatings were prepared by free-radical copolymerisation with MMA or by etherification of the resulting polymer and titanium tetraalkoxide.¹³⁴

Polytitanosiloxanes are prepared in one stage by simultaneous controlled hydrolysis (actually, cocondensation) of Si(OEt)_4 and $\text{Ti(OPr)}_2(\text{acac})_2$.¹³⁴ In this case, a ladder polymer containing Si--O--Si and Si--O--Ti units is formed. Their ratio depends on the conditions of the synthesis and can reach 10:1, respectively. This ratio determines the time of gel formation and the possibility of formation of fiber ceramics upon annealing of the material (500–900 °C).¹³⁵ The structures, the mechanism of growth and the properties of siloxane composites containing the silicon, titanium and mixed titanium-silicon phases (including those prepared *in situ*) were considered in more detail in the review.¹³⁶

The sol-gel method was used¹³⁷ for the synthesis of titanium–silicon nanocomposites based on perfluorosulfonate ionomers as well as for the preparation of nanosized particles with sizes 10–50 nm [from Ti(OR)_4 and Zr(OR)_4] incorporated into matrices of a copolymer of styrene and 4-vinylphenol,¹³⁸ *etc.* These approaches can also be used for the activation of surface polymers, for example, perfluorinated polymers [such as polytetrafluoroethylene (PTFE) or copolymers of tetrafluoroethylene with hexafluoropropylene] by their treatment with SiCl_4 followed by controlled hydrolysis.^{139, 140}

Metal (primarily, titanium and silicon) alkoxides are used as cross-linking reagents for many natural polymers (polysaccharides, cellulose derivatives, vegetable oils, *etc.*)^{141, 142}. These polymers contain highly active hydroxy groups, which can form oxopolymers *in situ*. Organic networks are also formed in the reactions of low-molecular-weight compounds containing several hydroxy groups (for example, anthracenobisresorcinol and its derivatives) with $(\text{Pr}^i\text{O})_2\text{TiCl}_2$.¹⁴³

Cocondensation of macromers containing trialkoxysilyl groups with the best known polymers [modified polystyrene (PS), polyoxazoline, polyimide, polyethylene glycol (PEG), polyetherketones, polymethyl methacrylate and derivatives of polytetramethylene oxide] is a convenient procedure for the preparation of telechelic polymer networks.^{106, 144–150}

The insertion of highly dispersed SiO_2 particles into a polymerised system is also widely used for the preparation of nanocomposite materials. Although a survey of this problem is beyond the scope of the present review, let us consider several most prominent, in our opinion, examples. In aqueous media, spherical SiO_2 particles possessing a high specific surface act as peculiar dispersing agents. In this manner, particles of a raspberry-shaped composite with sizes 100–300 nm were formed in polyaniline– SiO_2 or polypyrrole– SiO_2 systems.^{151–156} In the course of polymerisation initiated by the redox $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} - (\text{NH}_4)_2\text{S}_2\text{O}_8$ system, not only spherical but also fiber-shaped SiO_2 particles were introduced into polypyrrole formed.¹⁵⁷ The particle sizes vary within 80–200 nm as the SiO_2 : polypyrrole ratio changes.

Composites based on SnO_2 , which are used in lithography, are prepared by oxidation and cross-linking in films.^{158, 159} Tin-containing polymers (for example, poly(4-[(trimethylstannyl)methyl]styrene);¹⁶⁰ its synthesis was reported in Refs 161 and 162) are used as precursors of SnO_2 . Photoirradiation of polymers followed by their pyrolysis in air results in simultaneous formation of SnO_2 particles and a polymer network in which the polymers are incorporated. In this case, the C–Sn bonds are cleaved to form radicals of the benzyl and trimethylstannyl types. The former

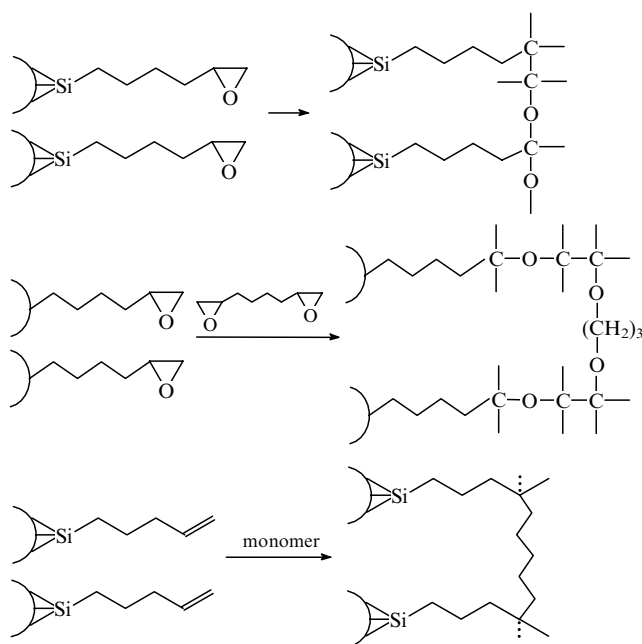


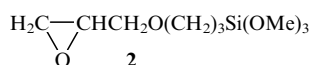
Figure 2. Use of functionalised silanes for cross-linking of organic and inorganic components of the system.

react with atmospheric oxygen on film surfaces. The latter undergo recombination to form networks.

Hybrid nanocomposites based on nanosized Au¹⁶³ and TiO₂ particles¹⁶⁴ were also prepared using reverse micelles. A surfactant (for example, didodecyltrimethylammonium bromide) was added to toluene with the resulting formation of reverse micelles into which AuCl₃ and a precursor gel, *viz.*, TEOS, were introduced. The LiBH₄–THF system was used as a reducing agent. Subsequent hydrolysis and condensation afforded Au particles impregnated into the wet gel. Their sizes depend on the H₂O : Si ratio and the concentration of the surfactant. After immobilisation on the surface of highly dispersed SiO₂ with the use of bifunctional aminosilane (MeO)₃Si(CH₂)₃NH(CH₂)₂NH₂ (see the review¹⁷), colloidal gold particles were stabilised with dodecanethiol.¹⁶⁵ Subsequent treatment of these particles with thiol resulted in the cleavage of bonds with SiO₂ and the particles became labile. Repeated immobilisation–stabilisation events led to the growth of two-dimensional highly ordered ~ 10 nm thick layers in which particles are linked together (Fig. 3).

It is best to prepare reverse micelles with the use of sodium bis(2-ethylhexyl)sulfosuccinate (SBES).¹⁶⁶ For example, Ti(OPr^{*i*})₄ was dissolved in reverse micelles, which were formed from isooctane and SBES and contained a calculated amount of water. In this case, the alkoxide slowly diffused into micelles and then was hydrolysed and condensed in these micelles as in microreactors. This procedure was used for the preparation of TiO₂ nanoparticles, which were extracted and dispersed in a solution of fluorinated polyimide. When a polymer–TiO₂ composite was deposited on a glass plate followed by thermal treatment (at 300 °C under an atmosphere of N₂ for 30 min), an optical film waveguide was formed. Therefore, one of the advantages of the preparation of these nanocomposites in a solution of a polymer is the possibility of formation of transparent films (in this case, yellow titanium complexes are not formed). The thermal stability of the above-described materials (4% of TiO₂) is almost identical to that of the initial polymer. This indicates that the thermal characteristics of the ‘host’ polymer remain virtually unchanged upon impregnation of TiO₂. In some cases, simple mixing of ingredients, *viz.*, a polyimide solution and a sol-gel precursor, which leads to phase separation, is sufficient to form a polymer–inorganic nanocomposite.

Compounds containing epoxysilane groups can form networks as well.^{167–170} Thus alkoxysilane (**2**) is a binder providing the compatibility of TEOS with polyacids.^{167, 168}



The component compositions of hybrid nanocomposites, which were prepared by the gel-sol method based on SiO₂ and an ethylene oxide–epichlorohydrin copolymer, were 71 : 29–29 : 71. Acid condensation of TEOS in a THF solution afforded an inorganic network.^{171, 172} These networks can also be prepared with the use of alkoxy derivatives of aluminium.

The morphology and fractal structures of these materials were studied. It is known¹⁷³ that the structures of aggregates are characterised by the fractal dimension D ($1 \leq D \leq 3$), which may have a meaning of an exponent in the equation relating the weight of the M particles to their characteristic size R

$$M \approx R^D.$$

For surface fractals with the uniform density, $D = 3$. The self-similarity or scale invariance of the fractal aggregate implies that the structure of the aggregate, on the average, remains unchanged on the interval as extended as is wished and any its portion is similar to the aggregate as a whole. When the surface is dealt with, the D value equal to 2 corresponds to the smooth surface and the D value equal to 3 corresponds to the maximum roughness.

The fractal dimensions of polymeric and colloidal samples of the TiO₂ aerogel with high values of S_{spec} (prepared by the sol-gel method and dried with CO₂ in the supercritical state), which were calculated by different methods, were compared. These values are virtually identical (2.6–2.8). The fractal surfaces of colloidal particles are only slightly less regular than those of polymeric aerogels.¹⁷⁴ This indicates that at the nanosize level, the morphology is determined in the early stages of the process and depends only slightly on the conditions of the synthesis, whereas on the mesolevel, it is the conditions of the synthesis that have a determining effect on the morphology.

Studies of the condensation of TEOS in a polysiloxane network demonstrated^{14, 136} that fractal models typical of solutions were not observed upon matrix polymerisation. Owing to large molecular weights of the matrix and the polymer formed, the entropy of the mixture decreases resulting in phase separation. Particular conditions are required to prevent phase separation in the system. However, phase separation always occurs when the concentration of SiO₂ is > 5%, which enhances the mechanical strength of composites. When TiO₂ nanoparticles were precipitated *in situ*, the maximum bulk domains (up to 5% of filling) were formed. These nanocomposites rank below systems with SiO₂ in strengths.¹⁷⁵

Of special note is the use of the sol-gel method for performing ‘template syntheses.’ In this case, nanocomposites are formed through ‘assembly’ from components under conditions of a strictly defined stereochemical orientation of the reagents. These conditions and primarily a small reaction volume (due to which reacting molecules can approach each other more closely than in

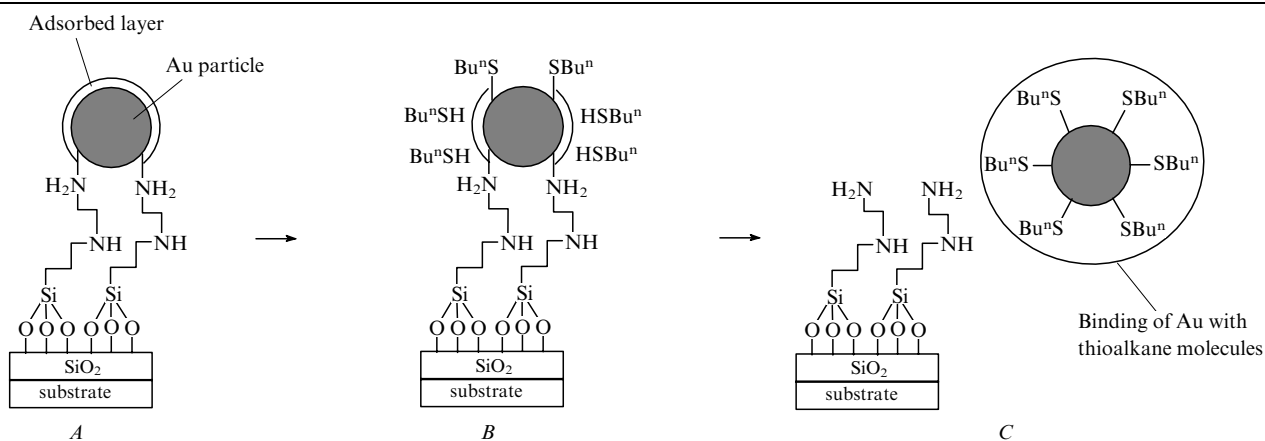
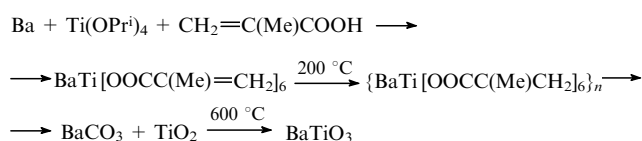


Figure 3. Preparation of hybrid materials with the use of reverse micelles: (A) immobilisation of colloidal Au particles; (B) exchange of alkanethiol molecules and cleavage of the Au–NH₂ bonds; (C) rapid regeneration of the layer on complete binding of Au particles.

solutions or in the solid phase) promote the so-called ‘mild’ template synthesis in the course of which the ‘assembly’ occurs under normal conditions (sometimes even at room temperature). For example, this procedure was used¹⁷⁶ for the preparation of tubular semiconducting nanostructures based on TiO₂ [from Ti(OPrⁱ)₄], commercial template membranes based on Al₂O₃ with the pore diameters of 22 and 200 nm¹⁷⁷ and fibrous structures based on ZnO (from zinc acetate¹⁷⁸) and WO₃.¹⁷⁹ These materials are excellent photocatalysts. The template synthesis is described in more detail below (Section V). The template sol-gel syntheses in fibres, nanotubes or micro- and nanoporous membranes were surveyed in detail in the review.¹⁸⁰ This procedure was used for the preparation of fibrous electrode materials based on V₂O₅¹⁸¹ and semiconducting oxide materials, such as MnO₂,¹⁸² Co₃O₄,¹⁸³ ZnO, WO₃, *etc.* The template synthesis of tubular nanostructural nanocomposites of the semiconductor-conductor type (as nanotubes or nanowires) was performed¹⁷⁶ starting from TiO₂ in Al₂O₃ pores followed by polymerisation of monomers.^{184, 185}

III. Preparation of nanohybrid multimetallic materials by the sol-gel method

Nanocomposites based on heterometallic ceramics, for example, on perovskite with the ABO₃ structure, can be synthesised by the sol-gel method. These materials (primarily, film and epitaxially oriented materials) possess specific ferro-, piezo- and pyroelectric properties and are widely used in electronics and optoelectronics.¹⁸⁶ The naturally occurring mineral perovskite CaTiO₃ has the pseudocubic crystal lattice. Perovskites, for example PbTiO₃, are generally prepared by calcination of a mixture of PbO and TiO₂, which is ground using a vibrational mill, at temperatures higher than 600 °C (synthesis *ex situ*). However, PbO is toxic and the presence of its phase in the final product is undesirable. The sol-gel technique for the preparation of perovskite PbTiO₃ is free from these drawbacks.¹⁸⁷ A mixture of Ti(OPrⁱ)₄, Pb(AcO)₂·3H₂O, ethylene glycol and citric acid taken in a ratio of 1 : 1 : 40 : 10, respectively, was stirred at 50 °C. Then the resulting citrate metal complexes were subjected to polymerisation at 130 °C and to pyrolysis at 300 °C. The resulting powdered precursor was calcined in air at 400–600 °C for 2 h to obtain thin PbTiO₃ films, which retained the properties of a bulk material. Different versions of the sol-gel syntheses of PbTiO₃ were described in the literature in detail. Thus polymeric films, which were prepared by mixing BaTiO₃ with solutions or melts of polymers, were studied.^{188, 189} However, in this case particles were nonhomogeneously distributed and their agglomeration occurred. An alternative hydrothermal procedure for the synthesis of these nanocomposites was proposed.¹⁹⁰ According to this procedure, BaTiO₃ particles prepared from Ba(OH)₂ and titanium diisopropoxide bis(ethylacetoacetate) at temperatures higher than 100 °C were grown in a polymeric matrix (in a polybutadiene–polystyrene block copolymer, *etc.*¹⁹¹). These materials can potentially serve as components of conducting compositions (see, for example, Ref. 192). Structurally homogeneous BaTiO₃ nanocomposites can only be prepared using the sol-gel method.¹⁹³ One of versions of this procedure involves solid-phase polymerisation of organometallic precursors followed by pyrolysis.¹⁹⁴



Polymerisation was also used for the preparation¹⁹⁵ of BaSnO₃ with the perovskite structure. The synthesis was carried out analogously to the synthesis of PbTiO₃ (see above) but at a different temperature and with the use of BaCO₃, SnCl₂·4.5H₂O, ethylene glycol and citric acid taken in a ratio of 1 : 1 : 40 : 10, respectively, as the starting compounds. Other multicomponent

ceramics of the perovskite type, *viz.*, SrTiO₃, NdAlO₃, SrBi₂Ta₂O₉ and superconducting ceramics YBa₂Cu₃O_{7-δ}, were also prepared by the sol-gel method (see below). The application of this method to the synthesis of these materials (the use of metallochelates and decomposition of organometallic precursors) was described in more detail in the study.¹⁹⁶ In the present review, let us note only that single-phase thin KTiOPO₄ films, which exhibit remarkable optical properties and high thermal stability, can be prepared according to this procedure; Ti(OEt)₄, KOEt and different sources of phosphorus [(EtO)₂P(O)(OH), (EtO)P(O)(OH)₂, P(OH)₂Me, P(OMe)₃, *etc.*], among which (BuⁿO)₂P(O)(OH) is an optimum source, are used as precursors.¹⁹⁷

Heteropolymetallates of the type of Keggin’s acids H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀, which are incorporated into organic–inorganic structures, may be assigned to the group of polymetallic nanocomposites.^{17, 117} These materials possess good electrochemical properties and can be potentially used in the holography. Nanocomposites based on these materials can be prepared according to two procedures, *viz.*, by mixing polymetallates (spheres of diameter ~ 1 nm) with TEOS [taken in a ratio of (2–6) : 10] and tetraethylene glycol or by introducing polymetallates into organosilanes.

Specific clusters, *viz.*, oxometallates containing W–O–Si units, which are inserted into the side chain of the polymer, were synthesised by the reactions of substituted trichlorosilanes RSiCl₃ (R = CH₂ = CH, CH₂ = CHCH₂, CH₂ = C(Me)CH₂ or CH = CHPh) with the polyanion K₄SiW₁₁O₃₉. In this case, cluster-containing monomers with composition [SiW₁₁O₄₀(SiR₂)₂]^{4–} were formed.¹⁷ Polymerisation was carried out under the action of radical initiators. The products were characterised by different methods, including ¹³C and ²⁹Si NMR spectroscopy. The yield of the polymer and the chain length depend on the reactivities of unsaturated groups R and increase in the series CH₂CH << CH₂ = CHCH₂ < CH₂ = C(Me)CH₂ < CH = CHPh. The structure of this polymer is schematically shown in Fig. 4. The syntheses of oxoclusters of transition metals Nb₄(μ₂-OMc)₄(μ₂-O)₄(OPrⁱ)₈, Ti₆O₄(OEt)₈(OMc)₈ (OMc is methacrylate) and Zr₁₀(μ₄-O)₂(μ₃-O)₄(μ₃-OH)₄(μ₂-OPrⁿ)₈·(OPrⁿ)₁₀(AllylAc)₆ (AllylAc is allyl acetoacetate)¹⁹⁸ by controlled hydrolysis of different metal alkoxides in the presence of complex-forming agents (OMc or AllylAc) were also reported. These compounds consist of the metal oxide nucleus and peripheral ligands, which can undergo polymerisation. The latter are responsible for the formation of a cluster network. The construction of stable ensembles of nanoblocks requires that clusters possess rather high lability and high reactivity. For example, the thermodynamical stability of titanium oxo clusters and their resistance to hydrolysis depend both on the size and the oxo(alkoxo) group:titanium ratio. With the aim of retaining

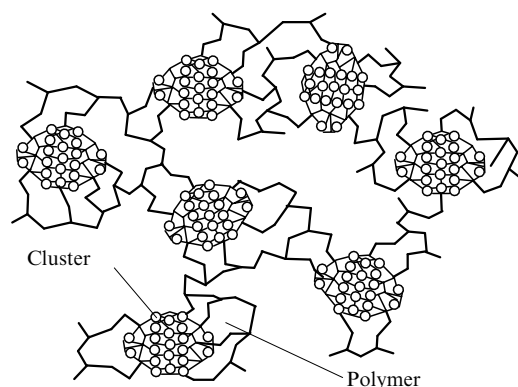
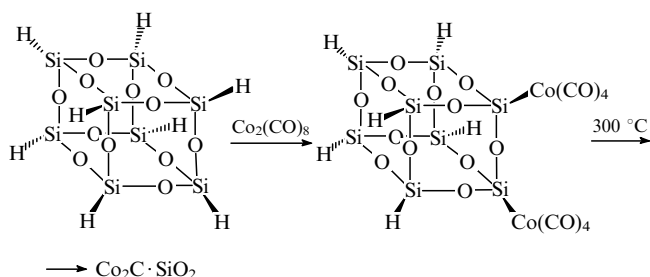


Figure 4. Structure of the hybrid polymer-inorganic material based on the {SiW₁₁O₄₀[Si(CHPh = CH)₂]^{4–} polyanion.

their molecular structures, polymerisation should be performed in anhydrous organic solvents.¹⁹⁹

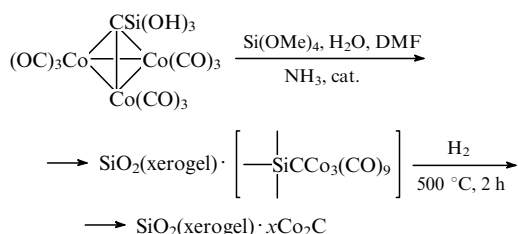
The syntheses of three-dimensional oxovanadium borophosphates with open frameworks^{200–202} and polyborozinylamines, which are precursors of metal-containing matrix composites containing metal borides and nitrides,²⁰³ are also available.

The possibilities of modification of materials prepared by the sol-gel method with different transition metals are being extensively studied (see, for example, Refs 204 and 205). For example, mesoporous materials M41S were prepared based on molecular sieves NCM-41 or MCM-48 modified with solutions of NH_4VO_3 or ZrOCl_2 in a mixture with polyoxoethylene stearate. Solutions of NH_4VO_3 or ZrOCl_2 acted as precursors of transition metal ions.²⁰⁶ Nanoparticles (50–60 nm) of cobalt carbide immobilised in a silicon matrix were obtained.²⁰⁷



Mesopores of MCM-41 matrices were modified²⁰⁸ with the *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ or $[\text{Co}(\text{en})_3]^{3+}$ complexes (en is ethylenediamine) stabilised by ammonium salts.

Hydrolytic condensation of cyclopentadienyltitanium chloride with silsesquioxane (the product of incomplete condensation of cyclopentyltrichlorosilane) followed by calcination of titanium-containing oligosilsesquioxane afforded microporous titanium–silicon oxides with S_{spec} of up to $780\text{ m}^2\text{ g}^{-1}$.²⁰⁹ In the stage of sol-gel polymerisation, metal clusters can be introduced into nanocomposites. Thus the trihydrosilyl group was inserted into a cluster with a known composition, *viz.*, $(\mu_3\text{-HC})\text{Co}_3(\text{CO})_9$, and then it was subjected to heterocondensation.²¹⁰



In the resulting xerogel, the unimodal distribution of the particles was observed. The sizes of the particles were 10–46 nm (the average diameter was 25 nm). The Os_3 , PtSn , Fe_2P , Co_2P and Ni_2P nanoclusters can be introduced into a composite analogously (by incorporation into a complex with a bifunctional ligand containing the reactive alkoxy- or hydroxysilyl group).²¹¹ The insertion of Pd^{2+} ions,²¹² Cu^{2+} ions,²¹³ *etc.* into poly(ethyltrimethylsilane) formed was described. The structures of organometallic–inorganic diblock copolymers, in particular, the structure of the ferrocenyldimethylsilane–dimethylsiloxane block copolymer, were studied.²¹⁴ In a hexane solution, the latter copolymer exists as long rod-shaped cylindrical micelles in which the iron-containing nucleus is placed in a ‘case’ (crown) formed from polydimethylsiloxane blocks. The micelle of this type comprises up to 2000 polymeric molecules and decomposes under the action of ultrasonics to form short cylinders containing ~ 700 molecules.

To perform heterogenisation of metal complex catalysts (see Section VIII), metal compounds are bound to an inorganic matrix

through a bidentate phosphorus-containing ligand of the $[\text{Ph}_2\text{P}(\text{CH}_2)_2\text{CO}_2]\text{EO}_x(\text{OR})_{3-2x}$ type ($\text{E} = \text{Ti}$ or Zr ; $\text{R} = \text{Alk}$).²¹⁵ Thus the reactions of such ligands with tungsten carbonyl afforded products $\text{W}(\text{CO})_5[\text{Ph}_2\text{PXE}(\text{OR})_{3-2x}]$, which are potential precursors for the sol-gel synthesis. Cocondensation of these precursors (analogous to the above-described condensation of metal clusters with TMOS) gave²¹⁶ xerogel nanocomposites with composition $\text{SiO}_2(\text{xerogel}) \cdot x\text{M}_y\text{P}_z$ ^{216–218} ($\text{M} = \text{Ru}$, Ga or In , $y = z = 1$; $\text{M} = \text{Pt}$, $y = 1$, $z = 2$; $\text{M} = \text{Fe}$, Co , Ni or Rh , $y = 2$, $z = 1$; $\text{M} = \text{Cd}$, $y = 3$, $z = 1$; $\text{M} = \text{Pd}$, $y = 5$, $z = 2$) and even bimetallic $\text{SiO}_2(\text{xerogel}) \cdot \text{Zn}(\text{Cd})\text{GeP}_2$ composites.²¹⁷ Immobilisation of the $[\eta^6\text{-PhSi}(\text{OMe})_3]\text{-Cr}(\text{CO})_3$ complex in a highly dispersed amorphous xerogel ($S_{\text{spec}} = 500\text{--}1800\text{ m}^2\text{ g}^{-1}$) in the course of sol-gel polymerisation (NH_4F catalyst) made it possible to prepare a single-phase hybrid of inorganic oxide and an organic network polymer containing (1,4-phenylene)siloxane bridges of the ‘nucleus–shell’ type.²¹⁹ Vacuum thermolysis (393 K, 24 h, < 1 Torr) of this composite even at 389 K resulted in elimination of carbonyl groups to form zero-valent chromium nanoparticles of sizes 1.0–10.0 nm in pores of the xerogel (Fig. 5). Under normal conditions, thermal elimination of carbonyl groups of the composite proceeded only at 400 °C. In the latter case, chromium in the low oxidation state was formed.²²⁰

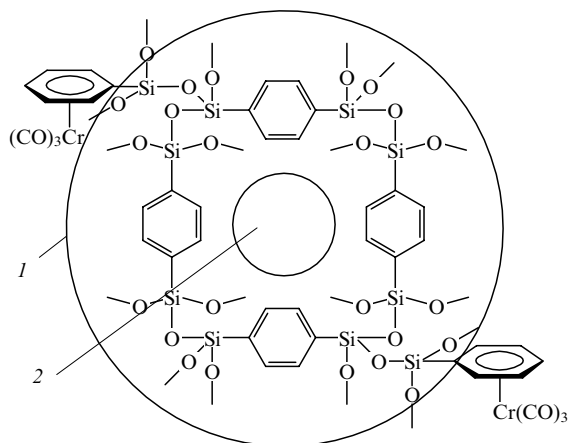
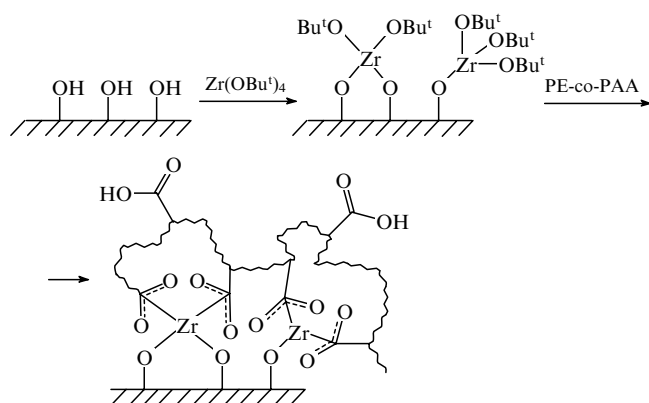


Figure 5. Structure of a single-phase hybrid of the ‘nucleus–shell’ type; (1) a shell, (2) a nanoparticle of zero-valent chromium.

Tricarbonylmolybdenum groups were introduced into the resulting polysilane according to the polymer-analogous conversion method. For this purpose, poly(methylphenylsilane) was treated with the $\text{Mo}(\text{CO})_3\text{Py}_3$ complex.²²¹

Nanolayer silanisation of inorganic surfaces of the TiO_2 , Al_2O_3 or Fe_2O_3 types, including the introduction of Fe_2O_3 into mesopores of silicates,²²² CaCO_3 , BaSO_4 , *etc.*, is widely used. Generally,^{223–226} a thin layer of silanol derivatives and a dimethylsiloxane oil are deposited on inorganic surfaces and heated to 250–280 °C. In this case, siloxane bonds are cleaved, the terminal groups of the polymer chain react with hydroxy groups of inorganic surfaces and the chains are cross-linked through methylene and siloxane bridges or oligomers. As a result, particles, which are stable to hydrolysis and extraction with different solvents, are formed. For example, $\text{Zr}(\text{OBu})_4$ modifies the aluminium surface.²²⁷ Zirconium groups are linked upon treatment with the poly(ethylene–acrylic acid) copolymer (PE-co-PAA) containing 5 mass % of units of acrylic acid.²²⁸



The adsorption properties of these materials are changed due to formation of a hydrophobic layer and the material becomes moisture-stable. When Ti and Au layers 5 and 50 nm thick, respectively, were deposited on the activated polydimethylsiloxane surface, ordered structures were formed.^{229, 230}

The coating of the surface of inorganic particles (including metals or their oxides) is often used in the technology of powder preparation to form structures of the 'nucleus-shell' type, which possess additional useful properties. Thus SnO_2 or In_2O_3 particles are coated with chelate polymers swelling in water (for example, those containing $\text{In}^{3+} - \text{SiO}_2$ or $\text{In}^{3+} - \text{Sn}^{2+} - \text{SiO}_2$ as well as Ag^+), which were preliminarily subjected to appropriate treatment. These particles exhibit the surface conductivity and are used for the preparation of thermally stable conducting films possessing antistatic properties, *etc.*^{231–233}

Therefore, several procedures for the insertion of a polymer into an inorganic material by the sol-gel method are available. Thus silanes containing two different functional groups can be used. One of these groups reacts with a monomeric unit of the macromolecule and the second group reacts with the sol-gel precursor resulting in the formation of a bond between the side group of the polymer and the sol-gel network. Sometimes special binding agents are additionally added. For example, the surface of highly dispersed SiO_2 was modified with aminobutyric acid and the resulting product was dried, dispersed in ϵ -caproamide and subjected to initiated polymerisation at 90 °C.²³⁴ If the concentration of SiO_2 particles is ≤ 5 mass % (the distance between the particles is 50–110 nm), they are homogeneously distributed in the composite. At concentrations of > 10 mass %, aggregation of particles starts. Layered nanohybrid materials (see Section V) were prepared²³⁵ by the reactions of $\text{Zn}(\text{OH})_2$, ZnO or a Zn/Al alloy with carboxylic acids or their oxychlorides. The 'guest': 'host' ratio in these composites varies from 0.75 : 0.25 to 0.9 : 0.1. The morphology of the particles changes from fibrous to platelet depending on the nature of the reacting components, the interlayer distance increasing in the range of 1.61–2.01 nm.

Recently, the sol-gel procedures for the preparation of ceramics based on aluminosilicates, *viz.*, carboxylates of the general formula $[\text{Al}(\text{O})_x(\text{OH})_y(\text{OOCR})_z]_n$, have been analysed.²³⁶ At the stage of formation, the $\text{M}(\text{acac})_n$ complex ($\text{M} = \text{Ca}^{2+}$, Mn^{2+} , Y^{3+} , *etc.*) can be additionally introduced into ceramics.^{237, 238} Metallic Co and Fe and their alloys, which were formed upon reduction of the corresponding nitrates with hydrogen, were dispersed in an aluminosilicate matrix. The matrix was synthesised by the sol-gel method from $(\text{BuO})_2\text{AlOSi}(\text{OEt})_3$ and possesses dielectric properties. In this case, nanocomposites with the particle size of ~ 20 nm possessing magnetic properties were obtained²³⁹ (Fig. 6).

One of new trends today in the field under consideration is to use carbon dioxide in the supercritical state as a solvent in the course of sol-gel polymerisation or in the stage of extraction of the resulting product. To perform the sol-gel process according to this procedure, the initial alkoxysilane is mixed with anhydrous 99% HCO_2H . Then polymerisation of the mixture is carried out in

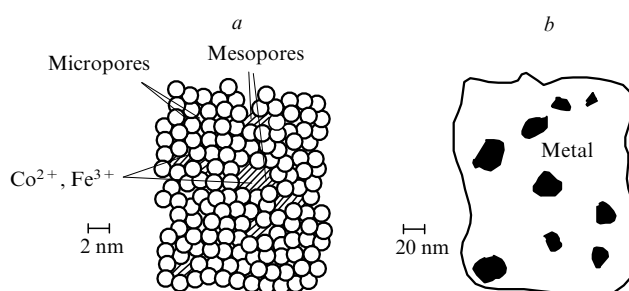


Figure 6. Diffusion and adsorption of metal ions in pores of the 'host' and the structure of the composite before (a) and after (b) thermal treatment.

supercritical CO_2 in an autoclave (40 °C, 41.4–55.2 MPa). The formation of the gel proceeds over 12 h and then CO_2 is slowly removed (8 h). This is favourable for the formation of highly porous monolithic composites with the meso- and macroarchitecture of the pores.²⁴⁰ Components, which sharply enhance the ability of SiO_2 to adsorb water, are also introduced at the stage of formation. For example, selective water adsorbents, such as CaCl_2 and LiBr , bind up to 53 mass % of H_2O .^{241, 242}

Colloidal dispersions of trimetallic $\text{Au}-\text{Pb}-\text{Cd}$ particles (the diameter is 33 nm) containing the gold nucleus with a 18 nm thick lead mantle are formed by γ -irradiation of salts of the corresponding metals.²⁴³ In this case (when nanocomposites contain three or more different metals, *i.e.*, they are multimetallic nanohybrids), studies of the structures of these particles is a challenging task. At the same time, these materials have already found use as precursors in the production of superconducting ceramics, special multicomponent steels, *etc.* When traditional approaches are employed, a polymer either is formed in a previously prepared inorganic matrix or is inserted into the latter. Multimetallic nanocomposites are formed either in a polymeric matrix *in situ* or simultaneously with the latter.

It is known that standard methods for the preparation of blends in the production of high- T_c superconducting ceramics (direct mixing of oxides, carbonates, oxalates, nitrates and other metal salts) give rather poorly reproducible results. This is due not only to the heterogeneity of grinding and mixing of the solid initial components but also due to complex physicochemical and mechanochemical conversions that occur in the course of the preparation of samples. As a result, microheterogeneities appear and different phases, including nonconducting phases, are formed resulting in low-quality high- T_c superconducting ceramics with a blurred superconducting transition (Meissner effect). A structurally homogeneous superconducting ceramic of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ type was formed when the initial components [for example, $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$] were mixed on the molecular level (in solution). After evaporation of the solvent (congruent evaporation), a homogeneous dispersion of a precursor of a high- T_c superconducting ceramic was obtained. With the aim of preparing composite materials, either a high- T_c superconducting ceramic is introduced into a polymeric matrix or this ceramic is prepared in the presence of a polymeric matrix. For example, in the first case, a dispersed high- T_c superconducting phase, *viz.*, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (ceramic Y-123), $(\text{Pb}_x\text{Bi}_{1-x})_2\text{Ca}_2.\text{Sr}_2\text{Cu}_3\text{O}_y$,²⁴⁴ or $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y$,²⁴⁵ with $T_c \sim 90, 110$ and 125 K, respectively, was introduced into a polymeric polychlorotrifluoroethylene, polyvinylchloride or rubber matrix. The ceramic content is 50%–75%. The optimum compositions combine advantages of a high- T_c superconductor (high T_c , good magnetic properties and magnetic levitation) and of polymers (mechanical strength, flexibility, simplicity of processing of products and resistance to atmospheric effects, aggressive media, *etc.*). In addition, the preparation of compositions allows one to eliminate drawbacks of a high- T_c superconducting ceramics, *viz.*,

the high porosity, the friability, the susceptibility to degradation, *etc.* However, rather large (micrometer) ceramic particles are inserted into a polymer according to this procedure.

In the second case, polymeric matrices containing metal ions dispersed on the molecular level are used (including the preparation of nanosized particles in the course of polymerisation or polycondensation). For example, citrates of different metals in aqueous solutions of acrylamide are polymerised in the presence of radical initiators and chain carriers (*N,N,N',N'*-tetraethylenediamine) to form a gelatinous phase.²⁴⁶ In this case, metal cations were trapped into a polyacrylamide gel much as occurs in the sol-gel synthesis. After calcination, ultrathin multicomponent oxide powders, such as $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ or LaAlO_3 , were obtained. The formation of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramics was performed with the use of acrylic or methacrylic acid as chelating ligands²⁴⁷ or with the use of polymer-salt solutions based on polymeric alcohols or acids, PEG or PVPr.^{248–250} The sizes of all salt crystals formed in the presence of any one polymer are substantially smaller than those obtained upon crystallisation of pure salt solutions. This is associated with complex formation in solutions as well as with adsorption of macromolecules on nuclei of crystallisation although it is not inconceivable that recrystallisation occurs simultaneously due to the presence of the concentration gradient of the components within the thickness of the film. Homogeneous films are most often formed because their formation occurs not only on the surface but also in the volume. It is essential that the final sizes of crystallites of the ceramics in the resulting powders should be approximately equal to their sizes in films.

The polymer-analogous conversion method was used for the preparation of the Y^{3+} , Ba^{2+} and Cu^{2+} complexes with polymethacrylic acid^{251,252} and of the YBC chelates with polyamides^{253,254} [gelatinisation with polyvinyl alcohol (PVA) can also be used].²⁵⁵ The superconducting ceramics based on these metalopolymers has $T_c = 80\text{--}92\text{ K}$, and the critical current density (J_c) is $150\text{--}160\text{ A cm}^{-2}$. Not only powders but also films and fibres can be prepared from these ceramics. (For this purpose, YBC-epoxy composites prepared from epoxide polymers are also suitable.²⁵⁶)

For example, long ($> 200\text{ cm}$) fibres 1 mm in diameter were formed from thermoplastic gels based on Y-123 ceramics and PVA.²⁵⁷ Calcined fibres have $T_c = 92\text{--}94\text{ K}$. These fibres form materials characterised by different J_c values depending on the degree of saponification (DS) and the content of the Y-123 ceramics in these materials.^{258–260} The critical current density has the minimum value when DS = 67 mol. % and the maximum value ($J_c = 3.5 \times 10^4\text{ A cm}^{-2}$, 77 K) when DS = 81 mol. %. This parameter is also affected by the conditions of treatment (calcination and pyrolysis) of samples, which is associated with the peculiarities of the distribution of the ceramics over fibres.

Nanocomposite materials based on high- T_c superconductors are also prepared by polymerisation of acrylic acid in a mixture with aqueous solutions of Y^{3+} nitrate and Ba^{2+} and Cu^{2+} acetates.²⁴⁷

One of the most promising approaches to the polymer synthesis of high- T_c superconductors involves copolymerisation of metal-containing monomers.²⁶¹ If metal ions are introduced into molecules of the monomer before copolymerisation, these ions are distributed in the polymer more uniformly. For this purpose, acrylates or acrylamide complexes of Y^{3+} , Ba^{2+} or Cu^{2+} were mixed in a molar ratio of 1:2:3, dissolved in a minimum amount of methanol, dried and subjected to solid-phase copolymerisation.²⁶² Acrylamide complexes of Bi^{3+} , Pb^{2+} , Sr^{2+} , Ca^{2+} and Cu^{2+} taken in a molar ratio of 2:0.3:2:2:3 were treated according to the same procedure (copolymerisation was carried out in concentrated aqueous solutions).²⁶³ The organic phase was calcined out from the resulting metal-containing copolymers. The properties of these high- T_c superconducting ceramics are shown in Fig. 7. Analysis of the temperature dependence of the electrical resistance (R) demonstrated that these ceramics behave as metals at $T < T_c$,

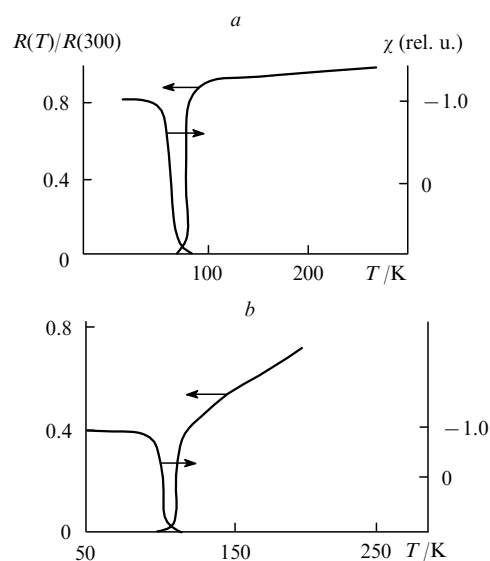


Figure 7. Temperature dependence of the electrical resistance and the magnetic susceptibility of high- T_c superconducting ceramics: (a) ceramics from a copolymer of Y, Ba and Cu acrylates; (b) ceramics prepared by spontaneous copolymerisation of acrylamide complexes of Bi, Ca, Sr, Pb and Cu.

although T_c of these ceramics are not as high as those of single crystals. It is known that the properties of polycrystalline samples in the normal state depend to a greater extent on the quality of intergrain contacts than on the structure of grains as such. The widths of superconducting transitions in the range of 0.1–0.9 of the value corresponding to complete resistance drop is no more than 2–3 K, which is close to the characteristics of the best samples of high- T_c superconducting ceramics. The character of the temperature dependence of the magnetic susceptibility (χ) is also indicative of the sharp transition and of the presence of the only superconducting phase. In this case, the complete volume of diamagnetic shielding of the phase, which is estimated from a lead reference compound, reaches 100%. The characteristics of superconducting bismuth cuprates are of particular importance. The reproducible synthesis of the latter is a challenging task. Generally, these compounds contain admixtures of a phase with $T_c = 85\text{ K}$ due to the microheterogeneity of the ceramics and the successive phase transitions $2201 \rightarrow 2212 \rightarrow 2223$. Products prepared by spontaneous copolymerisation are well reproducible single-phase samples with $T_c = 110\text{ K}$ and a critical current density of up to 240 A cm^{-2} . Apparently, this approach can also be used for the preparation of other single-phase materials in the nanocrystalline state.

The preparation of multicomponent steels of the M50 type (alloys containing 4.0 mass %, 4.5 mass %, 1.0 mass % and 0.8 mass % of Cr, Mo, V and C, respectively, and Fe as the remainder) may become an important field of application of nanostructured polymetallic materials. These steels are primarily used in aircraft construction for the preparation of supporting bearings, in gas turbine engines, *etc.*^{264,265} Generally, M50 steels contain substantial amounts of micron-sized carbon particles, which initiate the formation of fatigue cracks in the material of bearings. The mechanical properties of these structured materials would be expected to be improved as sizes of grains deposited on defects decrease (healing of microcracks); PVPr is used as a polymeric surfactant; $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{Et}_x\text{C}_6\text{H}_{6-x})_2$, $\text{Mo}(\text{Et}_x\text{C}_6\text{H}_{6-x})_2$ ($x = 0\text{--}4$) and $\text{V}(\text{CO})_6$ serve as precursors of the M50 steel. The process is carried out in dry decalin under ultrasonic irradiation (sonochemical synthesis). After removal of the solvent and the gaseous phase, colloidal particles have an average diameter of 7 nm and exist as a homogeneous alloy. Another procedure involves reduction of precursors of the M50

steel (FeCl_3 , MoCl_3 , CrCl_3 or VCl_3) with lithium triethylborohydride in THF followed by removal of solid LiCl by sublimation *in vacuo* at high temperature. Probably, these approaches will also be useful in the design of magnetic materials, for example, those based on polymetallic nanosized particles of the $\text{LaSrCr}_x\text{Ni}_{1-x}\text{O}_{4+\delta}$ type, *etc.* Thus a procedure for the preparation of the $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ceramics ($x = 0, 0.2, 0.4$ or 0.6) has been proposed recently.²⁶⁶ This procedure involves preliminary polymer synthesis consisting in binding of metal nitrates with a gel precursor from PEG ($M_w = 20\,000$) taken in certain ratios. Autoignition occurred at 300°C and NO_3 groups served as an oxidising agent. Subsequent thermal treatment of the combustion product afforded a homogeneous perovskite phase (see above). Its morphology and S_{spec} ($1-7\text{ m}^2\text{ g}^{-1}$; the sizes of crystallites were $24-150\text{ nm}$) depended on the reagent ratio and reaction conditions. A ceramic with cadmium and lanthanum additives with composition $\text{Pb}_{0.85}\text{Cd}_{0.05}\text{La}_{0.10}\text{Ti}_{0.975}\text{O}_3$ was prepared by the sol-gel method from metal acetates and $\text{Ti}(\text{O}i\text{Bu})_4$.²⁶⁷ Thin silicon films can be coated with this material in the stage of concentration of the solution (before drying). Subsequent thermolysis is carried out according to a standard procedure.

IV. Preparation of template synthetic nanobiocomposites by the sol-gel method

The sol-gel method provides considerable possibilities for the preparation of a series of nanohybrid materials in which biologically active macromolecules can be encapsulated at the stage of formation of ceramics, glasses and other inorganic composites (see, for example, Refs 268 and 269). The biological objects can be enzymes, catalytic antibodies, noncatalytic proteins, polynucleic acids and microbial, plant and animal cells²⁷⁰⁻²⁷² used in biocatalysis, for immunodiagnostics, as biooptical agents, various adsorbents, *etc.*^{268, 273-275}

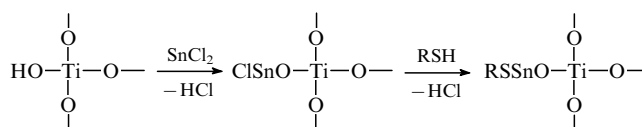
Biomolecules (active enzymes) were encapsulated into a sol-gel matrix for the first time in 1990.²⁷⁶ About 40 different types of hybrid bioceramic materials whose inorganic matrices contain silicon, titanium and zirconium oxides, TiO_2 -cellulose composites, *etc.* were described.²⁷⁷ Recently, bioceramic sensors, solid electrolytes, electrochemical biosensors, *etc.* have been surveyed in a review.²⁷⁸ Moderate temperatures and mild conditions of hydrolysis and polymerisation of monomeric alkoxides make it possible to trap proteins in the stage of formation of the matrix, thus preventing their denaturation. The high stability of the biomolecules trapped, the inertness, the large specific surface, the porosity and the optical transparency of the matrix facilitate heterogenisation because of which the sol-gel method of immobilisation is very attractive. Below are considered the principal approaches.

Proteins, such as copper-zinc superoxide dismutase, cytochrome, myoglobin, hemoglobin and bacteriorhodopsin, were encapsulated into a porous silica gel matrix prepared by the sol-gel method. The matrix effectively retains these biomolecules without loss in their enzymatic activity and changes in their spectral properties,²⁷⁹ does not preclude the approach of small molecules to the reaction centre and does not hinder transport of the reaction products. Heterogenisation of glucose oxidase and peroxidase, which are used as active solid-phase elements of glucosensors, was carried out according to the same procedure. The spectral characteristics of a gel containing oxalate oxidase and peroxidase are changed upon storage in aqueous solutions of oxalic acid.

Antibodies bound in such a manner are used in medicine, immunochromatography, immunosensors, *etc.* For example, immunoglobulins which are trapped retain their ability to bind external antigens from solutions.²⁸⁰ Antibodies 14D9 incorporated in sol-gel matrices catalyse different reactions, including hydrolysis of cyclic acetals, ketals, epoxides, *etc.*²⁸¹ The ability of the sol-gel matrix containing 10% of PEG and antiatrazine antibodies to bind atrazine was studied.²⁸² This matrix recognises

and binds atrazine and widely distributed herbicides in solutions. In this case, neither leaching of antibodies nor nonspecific physical sorption of atrazine on a ceramic matrix occur. A decrease in the activity was not observed for at least 2 months, while the activity in solutions decreased by 40% in this period. In addition, the use of the sol-gel method excludes the necessity of purifying immunoglobulin. It should be emphasised that these materials have other advantages, such as the enhanced thermal and pH stability, the possibility to monitor easily the enzymatic reactions both in pores and in the body of the matrix by spectral methods, the convenience of storage, the possibility of the repeated use, *etc.*²⁸³

Enzymes, which act as bioreactors (biodoped polymers), were immobilised according to the above-described procedure.¹²⁵⁻¹²⁷ For this purpose, chemically active terminal groups of enzymes and active bonds of dopants of the ceramics, for example of $\text{Sn}-\text{Cl}$, were used.²⁸⁴



R is an enzyme.

For example, alcohol dehydrogenase was immobilised into nanotubes of TiO_2 , which was prepared by template synthesis, according to this mechanism. This enzyme retained its ability to oxidise ethanol for more than 4 days (NAD^+ cofactor, phosphate buffer, pH 8).¹⁸⁰ Since nanotubes are open at both ends, this configuration allows one to use them as a flow reactor. These examples are large in number. They involve also covalent binding of antibodies with the aim of functionalising sol-gel films.²⁸⁰

Of considerable interest are procedures for the modification of matrices (including surfaces of metal oxides,²⁸⁵ silicates, siloxanes, hybrid sol-gel polymers) with different polyols (most often with glycerol) and their ethers followed by binding of trypsin, cytochrome *c*, superoxide dismutase, glucose oxidase, phospholipase D, *etc.*²⁸⁶ Bioencapsulants exhibit activity, which is almost identical to that of nonimmobilised enzymes. Besides, the former possess the high stability and exhibit the substantially better properties than materials prepared by the standard sol-gel method. Vinyl groups are grafted to the surface of SiO_2 particles (by treating aminosilica gel with acryloyl chloride) and copolymerisation of the resulting product with acrylamide and acrylic acid or *N,N*-dimethylaminopropylacrylamide is performed in the presence of a cross-linking agent and glucose oxidase.²⁸⁷ After removal of the protein from these nanocomposites, a molecular impression (template) remains. This template recognises glucose oxidases in protein mixtures.²⁸⁸ The so-called template approach based on the formation of porous silicate films about a specific reagent, which is then removed, using the sol-gel method was described. Template films prepared based on 3-hydroxytyramine²⁸⁹ have the higher affinity for this substrate than for structurally related molecules, including serotonin, dihydroxynaphthalene, *etc.*, and do not possess the affinity for negatively charged or large molecules, including the Tyr-Gly-Gly peptide. Apparently, the porosity of the film as well as steric, hydrophobic and electrostatic interactions play an important role in controlled penetration of different molecules through this film.

The formation of an organised material by the sol-gel method can be performed according to four procedures:²⁹⁰ (1) formation of self-assembling organic templates (transcription syntheses); (2) cooperative assembly of ensembles, *viz.*, template and building blocks (synergistic syntheses); (3) morphosynthesis in which organised nonlinear chemical environments, *viz.*, reaction fields (static, reorganisation, transition) are used for the construction of models;²⁹¹ (4) combination of these methods (integrated synthesis). This strategy (reaction ensemble $\rightarrow$ replication $\rightarrow$ metamorphism) resembles the general scheme of mineralisation. It can be exemplified by template-directed syntheses of ordered meso-

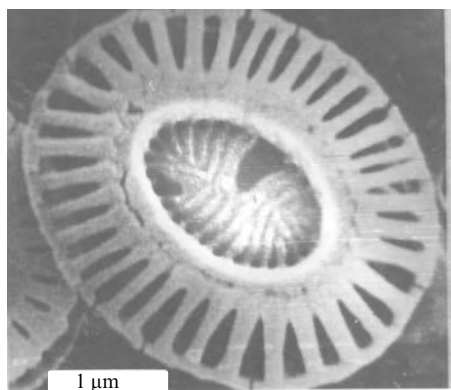


Figure 8. Electron micrograph of a coccus-like coat of the one-celled algae *Emiliana huxleyi*.²⁹²

forms and organoclays, microframework structures, including those with the use of bacterial templates. In particular, a coat of the one-celled algae *Emiliana huxleyi* consists of radially arranged hammer-shaped single crystals of calcite, which are crystallographically oriented and have a specific species form. The crystallographic orientation is retained in fossil casts, which is indicative of the control over nucleation on the molecular level (Fig. 8). This fact is most pronounced in the reproduction of hierarchic macrostructured organised silica gels. Multicellular fibres from *Bacillus subtilis* (Fig. 9) can serve as an example of scale organic 3D-templates.²⁹² Nanosized magnetic (Fe_3O_4), semiconducting (CdS) or TiO_2 particles, which has been preliminarily prepared, were introduced into macroscopic filaments upon swelling in colloids.²⁹³ Dried fibres (the diameter was 500 nm) were coated with a thin (30–70 nm) layer of aggregated colloidal particles. Negatively charged magnetic colloids exhibit the good permeability and reproduce the bacterial superstructure. Neutral CdS particles partially penetrate into the filament, but their major portion remains on the surface of the filament. Positively charged TiO_2 sols form only a surface coating. Removal of a bacterial component from a magnetic composite upon heating afforded structural collapse.

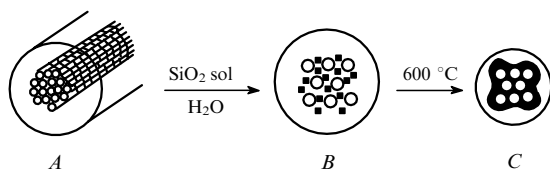


Figure 9. Scheme of formation of an organised macroporous SiO_2 structure with the use of bacterial templates, *viz.*, bacterial filaments with the structure of multicellular fibers (A), mineralisation of interfibre spaces of filaments (B) and the formation of macroporous replica upon drying (C).

To summarise, nanohybrid materials are widespread and are of considerable importance both in nonliving and living nature.^{2, 268, 273} Binding and decomposition of different organic compounds, the cycles of compounds and energy in nature and the formation of many useful minerals occur with the participation of nanohybrid materials. Outstanding possibilities are opened up in the field of the design of molecular-organised self-assembled systems, including nanobiomaterials. The protein environment is favourable to the preparation of complicatedly organised (both in form and composition) products. For example, perovskites (BaTiO_3 , SrTiO_3 or NaNbO_3) whose synthetic analogues are considered in Section III can be involved in processes of bioaggregation.²⁹⁴ It is believed^{295, 296} that finely monodispersed

precursors of high- T_c superconducting ceramics could be formed based on bacterial objects.

V. Intercalation of polymers into porous and layered nanostructures

Sometimes products prepared by the sol-gel method or by intercalation can be distinguished only by their past history. No less than 5000 studies dealing with problems of intercalation of organic, organometallic and inorganic compounds as well as with the properties of the resulting products were published up to 1994 inclusive,²⁹⁷ though the major body of information has been obtained during the last 5–10 years.

Natural layered silicates, the so-called smectites (or smectite clays) are most often used for the preparation of nanocomposites under consideration. Their structures, selected physicochemical properties and the nature of the active surface are considered in a review²⁹⁸ and monographs.^{20, 299} These are very widespread minerals to which hectorite and montmorillonite $[\text{AlMg}(\text{OH})_2(\text{O}_4)]^{5-}[\text{Si}_2\text{O}_5]^{4+}[\text{Na}, n\text{H}_2\text{O}]^+$ (MMN) with structures of the mica type belong. Crystals of MMN consist of alternating tetrahedral silicate layers of the cations condensed with negatively charged octahedral layers of metal oxides. However, unlike mica, the cations in these minerals are readily exchanged for other ions, including transition metal ions. The exchange occurs predominantly in layers containing solvated sodium cations. Intracrystal cavities can swell when they are filled with organic solvents. The degree of swelling depends on the nature of the cations within the layers and on the negative charge density on the silicate layers. Aluminosilicates and magnesiosilicates belong to clays whose nature is determined by the type of the octahedral metal. Within the lattice, Mg^{2+} and Al^{3+} can isomorphically replace Al^{3+} and Si^{4+} , respectively. The cations are hydrated and the layers readily swell and accommodate large cations or a substantial amount of water. In addition, most of inorganic oxides contain surface hydroxy groups, which actively bind metal ions. Crystalline rigid 'host' matrices with a controlled system of percolation nanometer-sized pores, which can be occupied by atomic or molecular 'guest' structures (clusters, nanosized particles, inorganic coordination polymers of the CdS type, large molecules of the C_{60} fullerene type and polymer units synthesised *in situ*^{20, 300–303}) are rather well studied. Thus intercalation of buckminster fullerene functionalised with ethylenediamine into a mica-like silicate of the fluorhectorite type has been described.³⁰⁰ Many procedures for the introduction of polymers in 'host' matrices are available. These hybrid nanocomposites are of technological interest because their properties are substantially improved compared to those of materials filled according to a standard procedure.^{304–306} For example, these materials prepared by thermal synthesis are generally metastable (in particular, due to flaking of the polymer from the inorganic component).

The properties of intercalated hybrid nanocomposites are determined by a number of characteristics, particularly, by the sizes of their inner open-pore systems. These properties were considered in many reviews (see, for example Refs 20 and 307–311). Intercalation systems are divided into two types according to their architecture and properties.³⁰⁹ The systems of the first type are characterised by the presence of rigid pores with a constant volume, the parallel isolation of lattice channels and the interrelation between the channels of the network. The location, the concentration and the spatial distribution of 'guests' are governed by the topology, the chemical nature and the reactivity of the inner surface of the 'host'. The matrix of the latter can be additionally dispersed and functionalised or long-chain surfactants can be intercalated into this matrix. In addition, the choice of 'guests' is limited by the minimum size of cross-linked channels, which leads to selective intercalation into induced spatial matrices (of the types of molecular sieves or membrane films). Systems of the second type are characterised by a low dimensionality of the

'host' lattice, *i.e.*, by the structures of the 'layer' or 'chain' types. As a result, the pores are 'flexible' and their sizes can be adapted to the size of the 'guest.' In layered systems, the basal (intralayer) space comprises ~ 5 nm. The thickness of the layer, for example, in perovskite varies in the range of 0.5–2.2 nm. From the viewpoint of the electronic properties, the matrix lattice of the 'guest' may have no effect on the intercalation–deintercalation process (this is true for lattices of dielectrics, *viz.*, of zeolites, layered aluminosilicates, metallophosphates, *etc.*, the intercalation behaviour of which is determined primarily by the acid–base and exchange properties). 'Guest' lattices possessing the electronic conductivity (semiconductors and metals) are a special case. Upon intercalation, redox reactions with electron (ion) transfer occur in these materials resulting in a substantial change in the physical properties of the 'host' matrix.

The inclusion of monomer molecules into pores of a 'host' followed by their controlled conversions into polymeric, oligomeric or hybrid-sandwich products (postintercalation conversions *in situ*) belong to the most interesting group of intracrystalline chemical reactions. This field has been rather well studied (see, for example, Refs 312–314). Intercalation of the appropriate monomer causes delamination and dispersion of 'host' layers, which is accompanied by polymerisation to form a linear or cross-linked polymeric matrix. This procedure was used for the insertion of polyesters,³¹⁵ PVPr^{316–318} and poly(ethylene oxide) (PEO)³¹⁹ into silicates and for the insertion of PVPr,³²⁰ polyimide^{321, 322} and poly(ϵ -caprolactam)^{305, 306} into kaolin. (When polymerisation was performed within kaolin, the resulting composites were nondelaminated products.) The most interesting hybrid nanocomposites were prepared from polyconjugated conducting polymers (which are often considered as materials for the preparation of battery plate), such as polyaniline,^{323, 324} poly(2-ethylaniline), poly(*p*-phenylene), polythiophene, polypyrrole^{323, 325} or pyrolysed polyacrylonitrile³²⁶ in different matrices.^{327–329} In this case, a great diversity of procedures can be used, *viz.*, the enclosure of a polymer into a gel,³³⁰ the use of salt solutions of the corresponding polymers [for example, polyaniline hydrochloride in an acid-methanolic solution or a sulfonium salt of poly(*p*-phenylene) soluble in many solvents], *etc.* The results of early studies in this field were summarised in the review.²⁹⁷ Thus oxidative polymerisation of pyrrole, dithiophene,^{331, 332} tetrahydrofuran³³³ and aniline³³⁴ in an FeOCl lattice was described. Intercalated aniline forms hydrogen bonds with chlorine atoms of the lattice, and polymerisation occurs along the (101) lattice diagonal. However, the conductivity of the resulting polymer is somewhat decreased. This lattice appeared to be suitable for oxidative polymerisation of aniline introduced from an aprotic solvent.^{331, 335, 336} The molecular formula of the resulting product was $(C_6H_5NH_2)_{0.28}FeOCl$.[‡] The zigzag polymer chains with $M_w = 6100$, which are comparable with the FeOCl lattice, are extended along the direction of the 'host' crystal and along the

hydrogen bonds between the NH groups and the chlorine atoms of the layers of the lattice. The $Fe^{2+} : Fe^{3+}$ ratio is $\sim 1 : 9$. The polymeric intercalate behaves as a *p*-type semiconductor (the conductivity of a single crystal is $1.5 \times 10^{-2} \text{ S cm}^{-1}$). Its prolonged oxidation in air afforded a mixture of polyaniline and β -FeOOH. Recently,³⁴⁰ it was proposed to use the α -RuCl₃ matrix, which is structurally similar to FeCl₃, for the preparation of lamellar nanocomposites of this type. The product of oxidative polymerisation of aniline in this matrix has the composition $(C_6H_5NH_2)_xRuCl_3$ ($0.5 < x < 0.6$). Its conductivity at room temperature is $\sim 2 \text{ S cm}^{-1}$, which is more than three orders of magnitude higher than that of the initial α -RuCl₃.

Postintercalation polymerisation of aniline was carried out in air at 130° in phosphate layers of α -Zr(HPO₄)₂·H₂O,^{341–343} VOPO₄,³⁴⁴ H₂O₂·PO₄·4H₂O,^{342, 345} layered acidic zirconium–copper phosphates,¹⁹ layered double hydroxides³⁴⁶ as well as in layers of $HM^1M^2O_6 \cdot H_2O$ ($M^1 = Nb$ or Ta ; $M^2 = Mo$ or W ^{347–349}), molybdenum sulfide,³⁵⁰ porous zeolites of the mordenite type,^{351, 352} MCM-41,³⁵¹ in layers of perovskite,³⁵³ mica-like silicates,³⁵⁴ *etc.*³⁵⁵ The resulting products are generally dielectrics. Polyoxometallates as 'host' matrices can serve as ideal models of 'molecular batteries' because they contain a small number (generally 6–8) of W or Mo atoms linked through oxygen bridges. Their spatial and electronic structures were adequately characterised.³⁵⁶ Chemical (electrochemical) polymerisation of pyrrole in Keggin's structures $H_3PM_{12}O_{40}$ ($M = W$ or Mo) was described.^{357, 358} Sometimes additional chemical reactions are carried out with the aim of converting these products into nanocomposites. For example, $(Bu_4N)_5Na_3[(1,5-COD)M \cdot P_2W_{15}Nb_3O_{62}]$ ($M = Ir$ or Rh ; 1,5-COD is 1,5-cyclooctadiene) was reduced with hydrogen in acetone.^{359, 360} These hybrid nanocomposites can be completed with phosphomolybdate anions (Scheme 3). The composition of the product corresponds to the formula $C_6H_5N \cdot (PM_{12}O_{40})_{0.116}$. Photochemical polymerisation of a diacetylene, *viz.*, 3,5-octadiyne, in layers of Mg, Mn or Zn phosphates was also reported.³¹¹

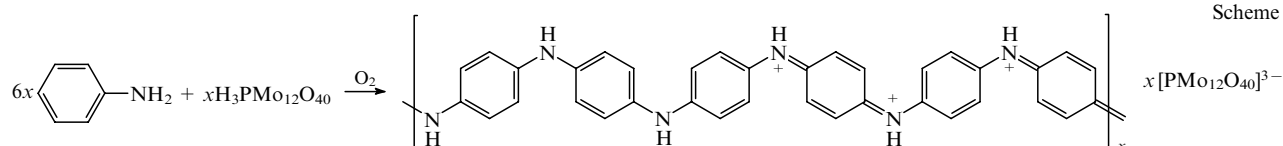
It can be suggested that under the appropriate conditions, monomers occupy virtually the entire space of pores or the whole interlayer space. Subsequent oxidative polymerisation ('redox-intercalation polymerisation')³⁵¹ was carried out in the presence of molecular oxygen (as an electron acceptor) and a redox-active 'host' (a catalyst of electron transfer). In this connection, layered silicates containing metal ions, which initiate polymerisation of an intercalated monomer, are of particular interest. Thus when Na^+ ions in hectorite are replaced by Cu^{2+} (sometimes by Fe^{3+}), styrene undergoes polymerisation¹⁶³ both in pores and on the surface. The polymer has a 'brush-like' structure, which indicates that the inorganic surface possesses an orienting effect. This effect decreases as the chain grows and moves away from the surface.

N-Vinylcarbazole is polymerised in MMN at 64 °C (in a benzene solution at 50 °C) due to the presence of cations in MMN.^{361, 362} The thickness of the intercalated layer of 'guest–host' particles is 33 ± 10 nm and the conductivity of this nanocomposite ($10^{-6} \text{ S cm}^{-1}$) is 10 orders of magnitude higher than that of polyvinylcarbazole.

Intercalated polystyrene exists in two forms.¹⁷⁵ One of them possesses the enhanced rigidity due apparently to a higher degree of ordering of the polymer. The improvement in physicochemical properties of intercalated polystyrene was observed also in the model PS–MMN system.³⁶³

Redox intercalation polymerisation of aniline, pyrrole and dithiophene with the use of a V₂O₅ xerogel affords polyconjugated

‡ The method consisting in quantitative removal of a polymer from an inorganic 'host,' its repeated dissolution and investigation could be an important technique for the analysis of polymers in these hybrid materials. However, although studies on the extraction of polymers from layered nanocomposites have been reported,^{6, 336, 337, 338} this field is poorly understood. Recently, rapid and quantitative extraction of PEO from the $K_x(C_2H_4O)_4M_{1-x/2}PS_2$ composite ($M = Mn$ or Cd) with an aqueous tetraethylammonium salt under normal conditions has been carried out.³³⁹ This process was analysed in detail and the kinetic regularities were revealed.



anisotropic polymers.^{364–366} Intercalation is accompanied by polymerisation. In this case, the chain growth initially occurs within the xerogel and is associated with transport of molecular oxygen. The V_2O_5 xerogel acts as a catalyst. A conducting polymer with different polyaniline: V_2O_5 ratios is formed with the participation of mixed-valence (V^{4+}/V^{5+}) ‘host’ lamellae ordered along one direction. The material consists of alternating layers of vanadium oxide and the polymer. Physicochemical studies demonstrated that polyaniline was formed as a salt. Ageing of the material in air facilitates partial oxidation of the inorganic framework and oxidative binding of polyaniline in the intralamellar space. The resulting polymer is ‘frozen’ due to the formation of a $NH\cdots OV$ hydrogen bond. A detailed analysis^{351, 367} of the insertion of aniline, its competitive polymerisation into MoO_3 and the formation of the nanocomposite $(C_6H_5NH_2)_{0.24} \cdot MoO_3$ structures, including those with the use of a low-temperature intercalation procedure,³⁶⁷ was carried out. It was found that polyaniline chains expand layers and change the potential surface thus decreasing the polarisability of the lattice.⁸ The polyaniline chains intercalated in MoO_3 oxide $(NH_4)_2S_2O_8$.¹⁹⁷ Oxidative polymerisation of aniline, pyrrole or thiophene monomers intercalated in layered aluminosilicates affords highly oriented ‘host–guest’ layers. It was found³² that radiation polymerisation of acrylonitrile and acrylic acid in MMN inclusion compounds afforded stereoregular (which are most likely syndiotactic) polymers.

Let us consider the most interesting procedures for the synthesis of one-dimensional nanocomposites based on intercalation into a matrix. An aqueous Au colloid (the particle size was 12 nm) stabilised with citric acid was introduced into pores of a Al_2O_3 filtration membrane (the average pore diameter was 20 nm) and oxidative polymerisation of pyrrole was performed *in situ* in these pores by adding an aqueous $Fe(ClO_4)_3$ solution.^{369, 370} After dissolution of the membrane in 0.5 M KOH, a suspension of one-dimensional colloid-polyppyrrrole nanostructures was obtained (Fig. 10).

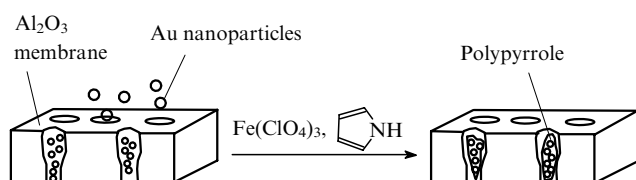


Figure 10. Template synthesis of one-dimensional Au–polyppyrrrole nanostructures in a Al_2O_3 membrane.

To construct solid light-sensitive solar cells, TiO_2 particles of size ~ 20 nm (prepared from $TiCl_3$, pH 2.5) are obtained at the surface of a photochemical electrode. Simultaneously, polypyrrole, which is formed upon electrochemical polymerisation of pyrrole adsorbed in electrode pores, precipitates on these particles.^{371, 372} These structurally controlled ‘templates’ are analogues of self-assembling supramolecular ensembles. Note that the procedure for the preparation of supramolecular systems for molecular recognition comprising chromophores, semiconductors and cluster aggregates, which perform special optical and electronic functions, is analogous to the above-considered preparation of nanobiocomposites.^{311, 373, 374}

One-dimensional parallel polyaniline chains prepared *in situ* can be encapsulated into structures with wide pores and large (the

diameter is ~ 3 nm) channels. In this case, the chains take a fibre shape and exhibit microwave conductivity.^{351, 375, 376}

An alternative to polymerisation *in situ* involves direct intercalation of macromolecules into layered structures, most often into silicates. The insertion of polymer molecules into layered ‘host’ lattices is of interest from different points of view. First, the construction of organic–inorganic polylayered composites becomes possible. Second, the intercalation physical chemistry by itself and the role of intercalation in the fact that the system gains electronic conductivity (for example, in the construction of reversible electrodes³⁰⁸) or improved physicochemical properties (nylon-layered silicate nanocomposites,^{377, 378} hybrid epoxide-clay composites,³²² nanomaterials based on hectorite and polyaniline, polythiophene or polypyrrole,³⁷⁹ etc.) are of interest.

The insertion of PEO into layers of mica-like sheet silicates in the reactions of a melt of the polymer with the ‘host’ Na^+ - or NH_4^+ -exchange lattice is one of a few examples of direct intercalation of polymers.³⁸⁰ Poly(ethylene oxide) is also inserted into lamellar networks of $V_2O_5 \cdot nH_2O$, MoO_3 ,^{337, 338, 381–383} $MnPS_3$, $CdPS_3$,^{381, 384} etc. Thus an aqueous solution of PEO ($M_w = 10^5$) reacts with an aqueous gel of $V_2O_5 \cdot nH_2O$ to form a composite after removal of water. In this case, the interlayer distance increases from 1.155 to 1.32 nm. Alkali metal ions react with PEO to form inclusion compounds, which can also be inserted into layers of ionic silicates, for example, into MMN. The distance between the layers of the PEO– Li^+ salt complexes intercalated in MMN is 0.8 nm, and the PEO chain adopts a slightly strained helicoid conformation.

Poly(ethylene oxide)– LiX systems find wide application as polymeric electrodes and solid electrolytes. However, these questions are beyond the scope of the present review and were considered in detail, for example, in the monographs.^{385–387} These systems are rather often used in combination with ceramic fillers (of the $LiAlO_2$, Al_2O_3 , TiO_2 , etc. types). Let us give only one example.³⁸⁸ Thus 10% of nanosized TiO_2 (13 nm) or Al_2O_3 (5.8 nm) particles were dispersed in acetonitrile with $LiClO_4$ and then PEO was added (the $LiClO_4$: PEO molar ratio was 1 : 8). The conductivity of the resulting polymer–inorganic nanocomposite is 10^{-4} and 10^{-5} S cm^{-1} at 50 and 30 °C, respectively. Recently,³⁸⁹ the preparation of a series of new hybrid polymer–inorganic electrolytes, which contain the aluminium atom in the main chain and Li^+ ions, by cocondensation of $LiAl(OR)_2H_2$ with organosilicon precursors has been reported.

The intercalation of polymers³⁹⁰ (PS,³⁹¹ PEO,³⁸⁰ polypropylene,^{392–394} etc.) from their melts into a silicate lattice is also a promising procedure. A molecular-dynamic model, theoretical calculations and the kinetics of formation of these intercalates were considered in the study.³⁹⁰ A new line of investigation involves direct hydrothermal crystallisation of silicate layers from a polymer gel.^{395, 396} This approach extends the range of intercalated polymers because it allows one to use compounds, which do not contain functional groups.

Activation of surfaces, layers and ‘host’ pores, including activation under the action of ultrasonics, is of importance in the processes under consideration. Thus Ni particles (10–40 nm) are deposited on submicrospherical silica gel.³⁹⁷ When a solution of $Ni(CO)_4$ in decalin was irradiated with ultrasonics, the Ni–C bonds were cleaved simultaneously with activation of the SiO_2 surface (the removal of adsorbed water, the cleavage of Si–O–Si bonds and the formation of free Si–O bonds). An alternative procedure involves the reaction of metallic nickel with activated silanol groups of the surface to form Si–O–Ni bonds. These centres serve as nuclei for further growth of Ni particles. Amorphous superparamagnetic Ni clusters were converted at 400 °C into a crystalline ferromagnetic material. This mechanism is realised to some extent for other dehydrated surfaces as well. For example, Al_2O_3 and metal carbonyls $M(CO)_n$ form Al–O–M structures.³⁹⁸ In such a manner gold nanosized particles were stabilised in a silica gel monolith.³⁹⁹ Thermolysis

§ Recently, the geometric structures and vibrational properties of complexes of polyenes with aluminium atoms as a constituent were studied by the *ab initio* quantum-chemical method in the Hartree–Fock approximation.³⁶⁸

of rhodium carbonyl on the Al_2O_3 surface afforded small Rh clusters.⁴⁰⁰

Nanocomposites self-assembled as $(\text{M}/\text{P})_n$ multilayers (M and P are nanosized oppositely charged layers of an inorganic component and a polymer, respectively) are worthy of special notice. These nanocomposites possess a variety of valuable properties, which makes it possible to use them, in particular, in the optical engineering for the production of displays.^{401–407} A great variety of procedures for the layer-by-layer assembly of polyelectrolytes and clays,^{408–413} lamellar zirconium phosphates⁴¹⁴ and colloidal metal particles^{415,416} were proposed. Using anionic MMN and positively charged poly(diallylmethylammonium chloride) (PDAMAC) as an example, the mechanism of formation of these materials on the surface of nanoplates from glass, quartz, silver, gold and even Teflon was considered in detail and the processes of defect formation were studied.⁴¹⁷ Successive submersion of plates into a solution of the P component or in a suspension of M leads to an increase in the number of layers (n). Each event is accompanied by an increase in the thickness of the P and M layers by 1.6 and 2.5 nm, respectively. The formation of multilayers involves several stages. First, adsorption on the substrate surface occurs, which is determined by electrostatic and van der Waals interactions. In this case, the structural hierarchy of the M layers provides limitless possibilities of their application as templates for a great variety of molecules and clusters,^{24, 418–422} which can be inserted between swollen layers or inside the M plates and can also be located on their surface. Second, the M component is strongly and irreversibly (which was confirmed by physicochemical studies) adsorbed on the oppositely charged polymeric electrolyte to form a very closely packed plane-oriented layer. Irregular M layers cannot provide complete coating of intercalated layers due to which overlapped stacks are formed. Interphase irregularities, which are independent of the nature of the substrate, exceed the thickness of the M/P layer. The control over the process can be performed by applying an external stress to the system in the course of self-assembly. In practice, a wide variety of these procedures were realised. For example, the PDAMAC polyelectrolyte and SiO_2 nanoparticles (the diameter was 25 nm) were successively deposited on the surface of a polystyrene latex. As a result of adsorption, a three-component polylayered material is formed (Fig. 11) in which the thickness of one, two and four SiO_2 –polymer layers are 60, 120 and 240 nm, respectively. The method of self-assembling of multilayers was also used for the preparation of nickel phthalocyaninetetrasulfonate–PDAMAC nanocomposites in which the average thickness of the M/P layer was 1.05 nm.⁴²³

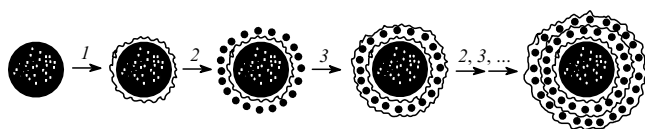


Figure 11. Scheme of self-assembly of a polylayer composite based on PS latex, SiO_2 and PDAMAC; (1) adsorption of polyelectrolyte, (2) adsorption of SiO_2 , (3) adsorption of a polycation.

Layered nanostructures were prepared⁴²⁴ with the use of liquid-crystalline polymers containing ionic groups; MMN or hydrotalcite $[\text{AlMg}_2(\text{OH})_2(\text{OH})_4]^+ [0.5 \text{ CO}_3, \text{ OH}, \text{ Cl}]^-$ was used as an inorganic component. According to different estimates, the average thickness of the M/P pair is 4.9 nm. It is believed that the electrostatic self-assembly promotes tight contacts between the components and the establishment of this molecular organisation, which allows one to prepare new types of liquid-crystalline structures with unusual properties. Apparently, the layer-by-layer assembly of aluminosilicate–polyelectrolyte nanocomposites is a promising procedure for the design of new membrane materials.⁴²⁵ In this review, hybrid nanocomposites, which were prepared, for example, by emulsion or gas-phase

polymerisation of traditional monomers (most often, styrene, MMA, aniline, ethylene, propylene, *etc.*) in the presence of different organophilic minerals, are not considered although these approaches are undoubtedly of interest by themselves (see, for example, Ref. 426). Thus emulsion polymerisation of the epoxy prepolymer (a product of condensation of equimolar amounts of bisphenol A with epichlorohydrin) in the presence of $\text{Na}^+ - \text{MMN}$ was accompanied by the insertion of the polymer into the basal space of the smectite clay, which expanded from 0.96 to 1.64 nm.⁴²⁷ A micelle with the monomer rather than the monomer as such was inserted into the body of the 'host,' which swelled in aqueous media. The resulting composite exhibits a higher thermal stability than that of the corresponding homopolymer. A hydrogel containing 3.5 mass % of MMN,⁴²⁸ which possesses the lower critical solution temperature ($\sim 32^\circ\text{C}$) than that of the nonmodified product, was prepared according to the same procedure (copolymerisation of *N*-isopropylacrylamide and *N,N'*-methylenebisacrylamide as a cross-linking agent in aqueous suspensions of MMN).⁴²⁹

Layered graphite inclusion compounds (LGC) were studied in detail. Graphite can be considered as an aromatic macromolecule. The number of aromatic rings in this molecule is ~ 1000 and the period of identity (the distance between the parallel planes) is 0.335 nm. Since the bonds between the parallel carbon layers in graphite are virtually absent (the energy of the interlayer interaction is only 16.8 J mol^{-1}), monomolecular layers of different compounds, including metal ions, can be inserted into graphite to form layered (laminated) compounds.⁴³⁰ Graphite inclusion compounds are generally prepared by the reactions of graphite with vapours or solutions of metals in strongly ionising solvents, with low-boiling chlorides or with cationic metal complexes. These compounds are divided into products of the first, second and subsequent stages of insertion depending on the number of carbon layers separating two adjacent layers of the metal inserted. The nature of bonds in these LGC depends on the nature of the metal. For example, in the cases of Fe, Co, Ni, Mn and Cu, van der Waals interactions exist. Sometimes when the π -electron density of graphite is transferred to the inserted metal layer, the carbon network of graphite becomes a peculiar polymeric ligand. In the case of alkali metals, this bond is formed as a result of electron transfer from the metal atoms to the conduction band of the adjacent graphite layer, *i.e.*, due to electrostatic interactions between the positively charged metal ions and free electrons of the conduction band of graphite (this problem was considered in more detail in Ref. 431).

In the course of reduction of inserted metal ions, they may partially leave layered stacks and reduction may occur on the outer surface of graphite. In such a manner nanosized particles, for example, of titanium are inserted into the imperfect lattice of graphite.⁴³² Many metals are inserted into graphite under high pressure in combination with shift deformation.⁴³³ Nanosized cobalt particles inserted into the graphite lattice according to this procedure exhibit the unusual magnetic and thermal properties.⁴³⁴

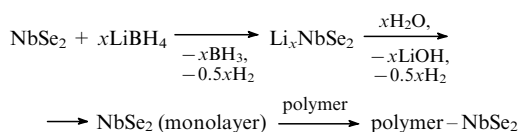
Therefore, intercalation chemistry provides virtually limitless possibilities for the construction of hybrid nanocomposites. Presently, the major effects attendant on the processes of formation of these materials are revealed. The structural organisation and the principal properties of these materials have been studied. The number of studies in this field is gradually increasing, which allows one to predict the design of materials of new types. For example, the synthesis of nanocomposites of a new interesting class, *viz.*, of hybrid materials containing azamacrocycles (gallium phosphates, *etc.*), has been reported recently.⁴³⁵ A start has been made on studies on intercalation (by the ionic exchange method) of nitrate groups of biomolecules, *viz.*, of nucleosidemonophosphates and DNA, into layered double hydroxides of the $\text{Mg}_2\text{Al}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ type ('anionic clays').⁴³⁶ Nanocomposites containing metal chalcogenide as a structural element ('host') are of special interest.

VI. Metal chalcogenide – polymer inclusion nanocomposites

Metal chalcogenide–polymer inclusion nanocomposites are rather well studied. The results of studies were surveyed in the monographs.^{437, 438}

Apparently, intercalation in the CdS structure has received much attention.⁴³⁹ Film composites are most generally prepared with the use of a solution of the corresponding precursor followed by the synthesis *in situ*.⁴⁴⁰ For example, $\text{Zr}(\text{OPr})_4$ in propanol was hydrolysed with an aqueous solution of acetic acid, and solutions of cadmium acetate and ammonium thiocyanate were added.⁴⁴¹ The composition was coated onto a glass support and treated as in the case of the sol-gel method (see Section II). The cryochemical treatment of gels impregnated with Cd^{2+} , Pb^{2+} or Zn^{2+} salts followed by sulfiding with hydrogen sulfide in the gaseous phase, afforded nanoparticles of sulfides with sizes from 3–7 to 30–100 nm in a SiO_2 matrix.⁷³ The formation of the dispersed CuS phase in a polyacrylic acid–polyvinyl alcohol polymeric matrix proceeds through the stages of formation of sulfur-containing copper complexes, associates, amorphous clusters and, finally, crystalline CuS nanoparticles.⁴⁴² The specific structure of the interfacial layer and limitations imposed by diffusion in the swollen polymeric matrix are responsible for the characteristic features of formation of small (~ 4 nm) particles, the character of their distribution in the matrix and the aggregative stability.

If the anion is readily polarised and the cation possesses strong polarising properties, the compounds with composition MX_2 have layered structures. The distinguishing feature of these layered materials (of the MoS_2 or TaS_2 types) characterised by the low charge density of the layer is their ability to decompose into nanosized building blocks under appropriate conditions and to form colloidal solutions. In molybdenum dichalcogenide, a layer of molybdenum atoms is located between layers of chalcogen atoms, and packs are formed from these triple layers. In this case, bonds within the packs are substantially stronger than those between two packs linked only through van der Waals forces.⁴⁴³ The exfoliation procedure has been developed in sufficient detail.^{444, 445} Plastic superconducting electromagnetic materials can be prepared based on nanocomposites.⁴⁴⁶ Intercalation of PVPr, PEO and PEG from aqueous solutions into monolayers of suspended NbSe_2 [it is known that the latter is of one the best superconductors among layered dichalcogenides ($T_c = 7.2$ K)] was reported.⁴⁴⁷ The compositions and the selected properties of the resulting nanocomposites are given in Table 1.



A polymer is inserted into the WS_2 phase according to the same mechanism.⁴⁴⁸

Table 1. Properties of intercalated polymer– NbSe_2 nanocomposites.

Composite	d / nm	Thermal stability in N_2 / °C	Conductivity / S cm^{-1}	T_c / K
(PVPr) _{0.14} NbSe ₂	2.40	310	140	7.1
(PEO) _{0.94} NbSe ₂	1.96	224	250	6.5
(PEG) _{0.80} NbSe ₂	1.88	233	240	7.0

In the case of delamination, the insertion of a polymer can occur according to the ‘host–guest’ mechanism. Then intercalated systems are deposited by removing the solvent or by increasing the concentration of the electrolyte. Direct intercalation of polyaniline into the interlayer space of MoS_2 ($d = 1.037$ nm) through formation of colloidal suspensions has been described.³⁵¹

The polypyrrole– MoS_2 nanocomposite, which is a product of oxidative polymerisation *in situ* under kinetically restricted conditions, is a p -type conductor. Its electronic conductivity is three orders of magnitude higher than that of the initial MoS_2 compound.⁴⁴⁹ Intercalation of PEO into a delaminated suspension of TiS_2 or MoS_2 was carried out.⁴⁵⁰ In aqueous solutions, nanocomposites of linear polyethyleneimine in layers of MoS_2 , MoSe_2 , TiS_2 or MPS_3 ($M = \text{Mn}$ or Cd)⁴⁵¹ as well as composites of polyethyleneimine or poly(styrene 4-sulfonate) in TiO_2 – PbS layers possessing semiconducting properties were prepared.⁴⁵²

Nanocrystals of semiconductors based on metal chalcogenides immobilised into polymeric matrices exhibit luminescent properties. This is primarily true for nanocrystals of CdSe ,^{453, 454} CdS – Ag ,⁴⁵⁵ ZnS and ZnS – CuS .^{456, 457} Composites based on ZnS – CuS , which contain crystals with dimensions ~ 2 nm in a polymeric matrix, were prepared by copolymerisation of acrylates of the corresponding metals with styrene followed by treatment of the solution of the resulting copolymer with hydrogen sulfide in chloroform.⁴⁵⁸ These composites possess good photo- and electroluminescent properties. It should be noted that a precipitate did not form from the resulting almost colourless organosol even after one year.

Metal chalcogenides with more complex layered structures, for example, PbNb_2S_5 and SmNb_2S_4 , can also be decomposed and subjected to intercalation.⁴⁵⁹ In polar solvents, one-dimensional ‘host’ phases form colloidal systems with MMo_3Se_3 ($M = \text{Li}$, Na or In). These systems contain monodisperse negatively charged condensed cluster chains $(\text{Mo}_3\text{Se}_3^-)_n$. The structures of these systems (which are also called pseudo-one-dimensional metals) have been described in sufficient detail.⁴⁶⁰ They are of interest in the design of materials with nanowire (or molecular-wire) morphology. For this purpose, block radical polymerisation of dilute (10^{-3} – 10^{-4} mol litre⁻¹) solutions of these ‘rigid rods’ in a solvating monomer (vinylene carbonate) is performed in the presence of a cross-linking agent.^{461, 462} The system rapidly solidifies, and the polymeric matrix provides capture, association

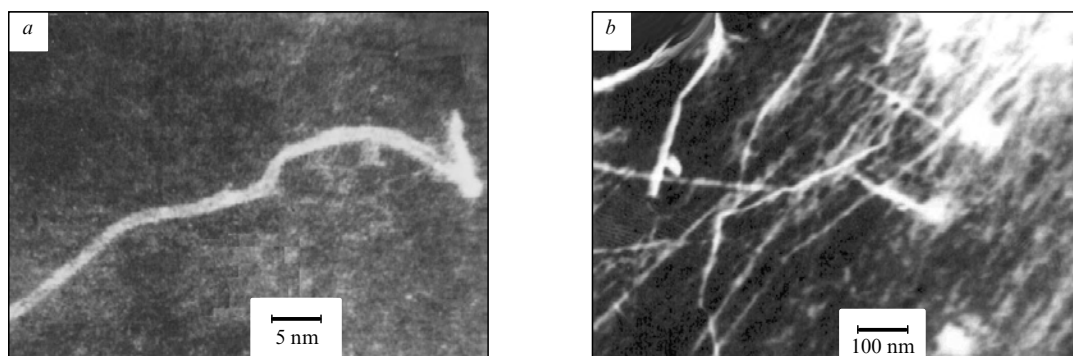


Figure 12. Electron microphotograph of a ‘nanowire’ (a) and ‘nanocable’ (b).

and isolation of the inorganic phase. The nanocomposite contains individual isotropic nanowires 0.6–2 nm in diameter and 5–10 nm in length. Polymerisation of more concentrated solutions (10^{-2} mol litre $^{-1}$) affords nanocomposites as oriented multiwires ('nanocables') 2–4 nm in diameter and ~500–1500 nm in length. Each 'nanocable' contains 5–20 'nanowires' (Fig. 12a, b). The molecular weight of the inorganic chain (wire) is estimated at $\sim 10^5$. The conductivity is 10^2 – 10^3 S cm $^{-1}$, *i.e.*, it is approximately equal to the conductivity of the (LiMo₃Se₃)_n film.

Therefore, intercalation of polymers into the interlayer space of chalcogenides is an extensively and fruitfully developing field of the technology for the preparation of nanocomposites, although many problems, particularly, those associated with the mechanism of insertion and 'guest–host' interactions are still not completely understood. In conclusion, let us give several more examples of these nanocomposites. Polymeric films based on nanosized particles (10–16 nm) of chalcogenides ZnS,⁴⁶³ as well as of Cu₂S–CdS–ZnS and different polymers, CdS⁴⁶⁴ and β -cyclodextrin were described. The inner diameter of the cavity of the latter is 1.53 nm,⁴⁶⁵ which is substantially smaller than the sizes of the nanosized particles. Nevertheless, monodisperse complex structures with the participation of β -cyclodextrin are formed. It was suggested⁴⁶⁴ that these structures are formed as a result of binding of monodisperse complexes with excess sulfide anions and cadmium cations to form CdS– β -cyclodextrin–S^{2–} aggregates.

VII. Metallopolymeric Langmuir–Blodgett films — self-organised hybrid nanocomposites

Metal-containing nanoparticles inserted into Langmuir–Blodgett films (LBF) belong to yet another promising class of materials for the preparation of nanocomposites. Procedures for the synthesis of self-organised inorganic component–surfactant composites, which have been developed in recent years, made it possible to prepare new two-dimensional composite materials.^{58, 466, 467} Generally, the sizes of the elements of these materials are no more than 2–10 nm.

Polymolecular LBF are used for the preparation of highly oriented ultrathin films possessing the special properties, which are determined by their supramolecular structures. Different sensor groups or their precursors possessing nonlinear optical properties can be inserted into these self-organised layers (in some cases, metal complexes, clusters or nanosized particles are inserted). Finally, LBF are used for modelling surface and biological processes (see, for example, Ref. 468). Supramolecular ensembles with mesosized periodicity (intermediates between materials of atomic and macroscopic sizes) are subjects of supramolecular chemistry, *viz.*, constructional chemistry of intermolecular bonds.

Although this line of investigation is still in a primitive state of progress, its methodology has already been developed. The technique for the preparation of Langmuir–Blodgett films was modified, when applied to this methodology. Heterogeneous polar nanolayers are prepared on the surface of a subphase (deionised water) at a given constant surface pressure π , which has the dimensionality mN m $^{-1}$. The pressure is measured using a Wilhelmy balance in a specially designed apparatus with two-section baths controlled by microprocessor electronic units and a computer with the use of the constant automated monitoring of the technological process.⁴⁶⁹ Successive transfer (by methods of Langmuir–Blodgett's vertical lift or Langmuir–Scheffer's horizontal lift) of these layers in the liquid-crystalline state to a solid support allows one to design sufficiently complex molecular planar structures possessing different properties. Metal particles in LBF can exist as a 'two-dimensional gas' (if their concentration on the surface is small and they do not interact with each other). Three-dimensional states, *viz.*, the 'gaseous' (the distance between the molecules is substantially larger than their sizes), 'liquid' (the

distance between the molecules is comparable with their sizes), 'liquid-crystalline' (the lability of the molecule in the plane of the monolayer is retained) and 'solid' states, are formed as the two-dimensional gas is compressed.

Two procedures for the formation of nanosized particles in these films are distinguished. The first of them is based on a combination of the principles of colloid chemistry and self-organisation and growth of monolayers.^{470–472} In this case, the formation of nanosized particles (for example, by chemical and photochemical reduction of aqueous solutions of metal salts) is performed in the presence of stabilisation agents and components forming LBF. The resulting layers act as specific templates.^{472–474} This approach is also of interest as regards studies of biomimetic processes of mineralisation, including studies with the use of the sol-gel method considered above.

The second procedure consists in deposition of LBF on the surface of stabilised nanosized particles and insertion of these particles into polylayers (with the participation of functional groups), including layers of an inorganic nature. For example, LBF based on amphiphilic Ru²⁺ complexes was immobilised on a monolayer of hectorite.⁴⁷⁵ In this case, lamellar films and polylayers were formed. Langmuir–Blodgett films with a specified organisation either were formed directly on the surface of colloidal particles or were formed on the water surface and then were transferred to a support of nanosized particles with the use of the Langmuir–Blodgett technique.^{476–479} Thus a gold hydrosol stabilised with 4-carboxy thiophene was immobilised on a monolayer of octadecylamine by the electrostatic method.⁴⁸⁰ The charge on the film was controlled by changing pH. Multilayer films with different densities of the Au–octadecylamine clusters with dimensions 10 ± 3 nm can be prepared according to this procedure; the films contain from 2 to 20 monolayers (the surface pressure in the monolayer is 25 mN m $^{-1}$ and the film area (*A*) is 0.37 nm² molecule $^{-1}$). Apparently, the method of immobilisation of nanosized particles on LBF has a number of advantages over the chemical insertion of metal ions into LBF followed by assembly of clusters, *viz.*, the deformation of films is excluded, ordering of the lamellar phase is not disrupted and various nanosized particles, including bi- and polymetallic particles, can be used by choosing appropriate hydrosol mixtures. When particles are immobilised on LBF, not only adsorption or chemical interactions occur, but also a higher recognition level is achieved. Examples are provided by self-organisation of monolayers of alkylsiloxanes, fatty acids, dialkyl sulfides or thiols on surfaces of Al, Au, SiO₂, *etc.*^{481, 482} Thus two processes occur on the mosaic Au–Al₂O₃ surface, *viz.*, recognition of the 'own' support (selective adsorption) and self-organisation of diphilic thiol (on Au regions of the support) and acid (on Al₂O₃ of the support).

However, the majority of studies were devoted to self-organised hybrid nanocomposites based on mononuclear complexes (in particular, on CdS), procedures for the assembly of nanosized particles from these complexes, investigations of the quantum dimensional effects typical of semiconducting nanoparticles, and practical applications of these nanocomposites.^{483, 484} It was demonstrated that a dispersion of CdS particles (2.65–3.4 nm) stabilised with dodecylbenzenesulfonic acid in CHCl₃ spreads over a water surface to form stable monolayers of nanosized particles.^{485, 486} According to the π –*A* compression isotherms, an increase in the π value leads to the transition from the 'gaseous' state to a close-packed monolayer of particles and, finally, to a polylayer. The resulting LBF are characterised by $A = 0.65$ – 1.1 nm² particle $^{-1}$, which is close to the corresponding values for the hexagonally packed rigid spheres (0.608 – 0.887 nm² particle $^{-1}$). The transfer of these monolayers to a solid support by the Langmuir–Blodgett method produces polylayers of dimensionally quantised CdS clusters. Their optical density increases linearly as the number of monolayers transferred increases.

The formation of nanosized semiconducting particles in LBF *in situ* by the reactions of metal ions with H₂S or Na₂S has been

One of the promising approaches of electrochemical synthesis involves the formation of two-dimensional (Langmuir) monolayers of nanosized particles under monolayer matrices of surfactants, which are present on the surface of an electrolytic solution,

Classical LBF can be prepared with the use of not only low-molecular-weight but also polymeric systems. In this case, with the aim of imparting the hydrophobicity to the chain, thus providing the formation of monolayers, the chain is functionalised either using polymer-analogous conversions or by grafting side chains, which can respond to the external factors. As in the case of the preparation of nanocomposites of other types, polymerisation of functional monomers and their copolymerisation with monomers, which serve as spacer units, are also used. In principle, diphilic LBF based on polymers have advantages over polymolecular films based on low-molecular-weight compounds, if for no other reason than their higher stability. These materials support the required density of a monolayer upon formation of a film (an



equilibrium pressure of spreading of monolayers is a more rigorous criterion for their thermodynamical stability). To solve some applied problems, it is necessary to introduce functional groups of different types into LBF monolayers. For example, components of a redox pair can serve as such functional groups. However, serious limitations emerge when employing low-molecular-weight reagents because diphilic compounds are not mixed at the molecular level and phase separation occurs. The use of polymers allows one to solve this problem rather readily. The effect of the composition and the structure of polymers and copolymers as well as of the external conditions on the formation and properties of organised polymeric monolayers and LBF on surfaces of liquids and solids were analysed in detail in a review.⁵⁰³ The formation of LBF was performed with the use of polymeric metal complexes based on porphyrins and phthalocyanines.^{504, 505} For example, the diphilic properties can be imparted to polymers by copolymerisation of long-chain α -alkenes with maleic acid, maleic anhydride and other compounds⁵⁰⁶ because the carboxyl group is a convenient fragment for binding a metal complex. When reagents, such as 4-aminomethylpyridine, are used for the opening of the anhydride ring, groups capable of providing donor-acceptor bonding of metals possessing coordination vacancies are formed in the polymer. This procedure was used for binding tris(phenanthroline)iron(II) sulfate or bis(salicylidenoaminopropyl)aminocobalt(II) to diphilic copolymers, *viz.*, to copolymers of maleic acid-pyridinemonoamide with octadecene or maleic acid-picolinemonoamide with *N,N*-dioctadecylacrylamide.⁵⁰⁷ The dependence of the surface tension π on the area of the monolayer per molecule (A) at the air-water interface is shown in Fig. 13. The type of isotherm for the film formation is determined by the concentration of a metal complex because its dimensions are substantially larger compared to the area of monomeric units (it is assumed that a cubic complex molecule is located nearly parallel to the water surface). At concentrations of the complex higher than 10^{-7} mol litre $^{-1}$, this fact is of considerable importance in the organisation of a monolayer. After compression ($\pi = 25$ mN m $^{-1}$), a stable homogeneous monolayer is formed. However, the stability is lost at concentrations of $\sim 10^{-4}$ mol litre $^{-1}$.

An important point is that one monolayer as a component of a multilayer system can contain metal complexes of two different types. Their bonding by two functional groups possessing opposite properties prevents phase separation.

Recently, the preparation of mono- and polylayer LBF based on a copolyimide the chain of which contains carbazole groups (as an electron donor) and copper phthalocyanine has been reported.⁵⁰⁸ The stack molecular organisation of the layers and

small intermolecular distances in these LBF ensure the high lability of the charge and impart the good photoconducting properties to LBF.⁵⁰⁹

Regular ensembles of nanocomposites organised in LBF multilayers are also constructed through electrostatic interactions between charged sol nanoparticles dispersed in a subphase and charged monolayers of the surface (for example, between anionic nanoparticles and a cationic polyelectrolyte).⁴⁰⁸ This procedure was used for the synthesis of regular nanowire TiO $_2$ -PVC-arachidic acid composites (PVC is polyvinylcarbazole) based on cross-linked polycationic PVC, which was prepared by electrochemical polymerisation of *N*-vinylcarbazole in the presence of NaClO $_4$, and a sol of thallium oxide (*n*-type semiconductor).⁵¹⁰ The resulting polymeric layer (2.7 nm) serves as a peculiar template coated with regularly organised TiO $_2$ particles (3.2 nm). The resulting 5.5 nm thick monolayers can be transferred layer-by-layer to the hydrophobic surface ($\pi = 25$ mN m $^{-1}$). Evidently, this method will gain wide acceptance because electrochemical polymerisation allows one to produce a large number of positively charged conducting polymers, for example, polyaniline, polypyrrole, polythiophene, *etc.*⁵¹¹

Apparently, this mechanism is also realised in the formation of self-organised layers of TiO $_2$ on SO $_2$ -functionalised polymer surfaces⁵¹² as well as in the preparation of ordered TiO $_2$ layers on poly(sodium 4-styrenesulfonate) (PSS). TiO $_2$ particles (~ 3 nm), which were prepared by acid hydrolysis of TiCl $_4$, formed organised layered structures on surfaces of polymers of the cationic type, *viz.*, on superthin (~ 1 nm) PSS or PDA-MAC.⁵¹³ Optically transparent LBF organised on the molecular level and containing up to 120 layers (60 bilayers) were formed on surfaces of various substrates, *viz.*, metal, silicon or a polymer cleaned with a 5% *N*-2-(2-aminoethyl)-3-aminopropyltrimethoxysilane solution. The thickness of the bilayer was estimated at 3.6 nm. It is expected that this procedure will allow one to realise various combinations of materials with semiconducting metal-dielectric structures containing nanosized units of the *p-n*-, *p-n-p*-, *n-p-n*-, *etc.* types. Recently, polylayer (2–12 layers) films of hybrid nanocomposites with the $N \rightarrow Cd$ coordination bond have been prepared by the reaction of poly(4-vinylpyridine) (P4VP) with nanosized particles of cadmium sulfide.⁵¹⁴

Nanocomposites of yet another type, *viz.*, clusters in a Langmuir monolayer, are of interest for the design of metal-film materials used in the electronics as well as for the modelling of structures of fixed catalysts. For example, the reaction of Os $_3$ (CO) $_{11}$ (NCCH $_3$) with self-organised layers of (3-mercaptopropyl)trimethoxysilane on a gold surface resulted in the disruption of the well-organised thiol surface to form cluster aggregates (the diameter was 1.0–2.2 nm).⁵¹⁵ Layer-by-layer adsorption of one- and two-dimensional complexes of the [Cd $_4$ L $_4$] $^{8+}$ type, which are characterised by the octahedral coordination, on monomolecular poly(ethyleneimine hydrochloride) and polystyrenesulfonate films on silicon can be considered to be an efficient method for the preparation of new metal-containing supramolecular thin films.⁵¹⁶

Particular attention is given to metal clusters in LBF deposited on the surface of highly oriented pyrolytic graphite (HOPG). Their application allows one to solve many catalytic problems as well as to prepare stable reproducible tunnel nanostructures. The Rh $_4$ (CO) $_{12}$ and (NEt $_4$) $_2$ [Pt $_{12}$ (CO) $_{24}$] $^{2+}$ clusters sorbed on HOPG from solutions of organic solvents were studied by scanning tunnel microscopy.⁵¹⁷ Under laser irradiation, these clusters underwent decarbonylation and transformation to highly dispersed Pt crystallites of dimensions 1.8×0.5 nm bound to the graphite surface.⁵¹⁸ The procedure for the deposition of isolated 'naked' silver clusters on the HOPG surface with the topography characterised by planar dimensions of 3–5 nm and the height of 2–3 nm and the technique for the 'assembly' of their ligand shell from PPh $_3$ were developed.⁵¹⁹ The voltammetric characteristics of individual clusters on the surface of freshly cleaved HOPG were measured. The insertion of the clusters into monolayers of stearic

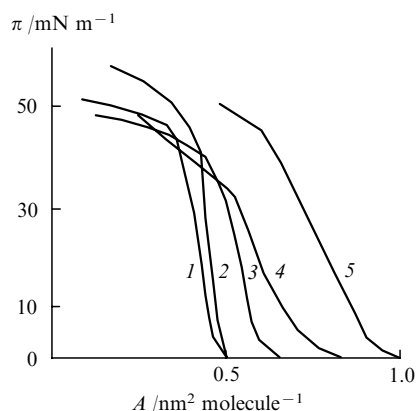


Figure 13. Isotherm of the film formation of maleic acid-pyridinemonoamide-octadecene copolymers on different sub-phases: (1) an aqueous solution of an alkali with pH 10, (2–5) solutions of [bis(salicylideneaminopropyl)amine]cobalt(II) with the concentration/mol litre $^{-1}$: (2) 10^{-7} , (3) 10^{-6} , (4) 10^{-5} and (5) 10^{-4} .

acid and their transfer to the HOPG surface also afforded cluster-containing LBF.⁵²⁰ In the resulting monolayer, the cluster molecules form an ordered two-dimensional lattice. By this means the problem of fixing of clusters on the surface was solved and the reproducible one-electron mode of tunneling was realised at room temperature. The regularities of the insertion of cluster molecules (Pd₃, Pt₅ and Pd₁₀) into LBF and their voltammetric characteristics were analysed in the study.⁵²¹ A multilayer LBF was transferred from magnesium stearate (from a monolayer of stearic acid to the surface of aqueous solutions of MgCl₂) to the HOPG surface in the disrupted state; the surface per molecule is 0.15 nm², $\pi = 36$ mN m⁻¹ (see Ref. 494).

The above-considered examples demonstrate that metal-containing Langmuir–Blodgett films, including those based on nanosized particles and clusters, are of considerable interest for the preparation of hybrid organised nanocomposites.

VIII. Major fields of application of hybrid nanocomposites

When considering synthetic problems, we have already drawn attention to the properties of the resulting nanocomposites and to the possibilities of their practical application. Undoubtedly, these problems merit detailed consideration. In the present review, only the major problems are briefly analysed.

Hybrid nanocomposites are primarily used for the preparation of plastic materials possessing semiconducting and superconducting properties. Among them are nanowires on polymeric matrices, films with special properties,³⁰⁹ and different-purpose ceramics, including membranes, luminophors, antireflection and reflecting coatings on optical units, carriers and catalysts, reinforcing agents for plastics and rubbers, binders, adsorbents for pharmaceutical and cosmetic industry, *etc.*^{116, 522–527} The recent review²⁷⁸ devoted to the use of materials prepared by the sol-gel method in electrochemistry includes more than 300 references. Optical waveguides were constructed based on hybrid polymer-inorganic nanomaterials, which were prepared by the same procedure and possess improved thermal and mechanical properties compared to the starting polymers.^{164, 528, 529}

Nanoparticles, for example SiO₂, TiO₂, CdS, CaCO₃ and BaSO₄, including those formed by the sol-gel method, are used as specific fillers, because the properties of materials are noticeably improved at a substantially lower concentration in a matrix than those prepared with the use of standard fillers. Thus when fillers are inserted into composites by mechanical dispersion using mixing equipment (the size particles is ~ 1 μ m), it is necessary that up to 40 mass %–50 mass % of the filler should be taken for 100 mass % of polyisopropylene to attain the required reinforcing effect, whereas the same effect is achieved by the insertion of only 0.6 mass %–0.8 mass % of a filler *in situ*.⁵³⁰ Highly filled (up to 75%) composite materials based on nanosized particles of the high-T_c superconductor Tl₂Ba₂Ca₂Cu₃O_y ($T_c = 125$ K) and polychlorotrifluoroethylene possess improved physicochemical and thermal characteristics and stability to atmospheric moisture.⁵³¹ These materials can be used for the design of cryoelectronic instruments, levitation equipment and magnetic screens.

Recently, efforts have been made to describe the viscoelastic properties of a composite taking into account the specificity of interactions between segments of the macromolecules and the active centres of the nanoparticles. The Kerner equation, which relates the elastic modulus of a composite upon simple extension to the portion ϕ of the inorganic phase, was modified⁵³² when applied to systems with strong interactions between nanoparticles and a polymer. Based on scaling theory, the equilibrium mechanical properties of a complex of colloidal particles and macromolecules some segments of which are adsorbed on active centres on the surface of particles (which are 'polynodes' of a network of the nanocomposite) were described.⁵³³ Under deformation and changes of the temperature, some segments leave the surface and the fragment of the macromolecular chain linking the surfaces of

two particles is increased by the same number of the segments. If this fact is taken into account, two nontrivial conclusions can be made: (1) the elastic properties of the composite are not only determined by the volume fraction of filling but are also inversely proportional to the linear size of the particles; (2) the shift modulus of the nanocomposite, unlike the shift modulus of nonfilled polymeric networks, does not approach zero as the temperature is extrapolated to zero. These conclusions agree well with the results of studies of the relaxation mechanical properties of the composite as well as the dependence of its viscosity on the molecular and structural parameters, such as the energy of interaction between the segment of the macromolecule and the active centre of the nanoparticle, the number of segments of the macromolecule, their size, the ϕ value, the particle size (the diameter is ≤ 30 nm) and the temperature.⁵³³

Let us briefly consider the conducting properties of hybrid nanocomposites. These properties are manifested only with particular inorganic component: polymer ratios when current-conducting channels of fractal metal-containing clusters are formed in a polymeric matrix for one reason or other. The highest conductivity is achieved when the composite is converted into a network of interrelated current-conducting chains, *i.e.*, it has a percolation structure (see, for example, Ref. 534). To put it differently, critical concentrations of the filler ϕ_{cr} (the percolation threshold) exist above which ($\phi > \phi_{cr}$) the conductivity sharply increases.

With a knowledge of the percolation threshold, the minimum necessary filling of conducting composites can be predicted. For example, ϕ_{cr} for epoxysilicon resin filled with spherical particles of dispersed nickel is 0.25 and the critical parameter (X_{cr}) determined by the number of bonds at conducting nodes in the lattice of the solid is 0.30.⁵³⁵

The conductivity of metallopolymeric nanocomposites is substantially affected by the dispersity of an inorganic component. Different nanocomposites are characterised by different relationships between the conductivity and the metal content. The percolation threshold of composites based on layered pyromellitimide films containing inserted silver particles is attained when the filler content is > 9 mass %. At the same time, when silver nanosized particles (10–15 nm), which are prepared in the course of thermolysis of a prepolymer [a solution of silver acetate in poly(pyromellitimide acid)], are uniformly distributed over a film, the composite does not take on the conducting properties at the same filler content. The dielectric characteristics of films ($\sigma = 10^{-15} - 10^{-12}$ S m⁻¹) are retained at a high level, which is in many respects associated with the presence of a substantial fraction of dielectric polymeric interlayers between conducting particles of the filler.

It is possible to enhance the conductivity of polymeric composites as a result of the formation of a filler as 'nucleus' (conductor or dielectric)–'shell' (conductor) constructions. This is of practical interest primarily in the technology of the production of glues and varnishes. For example, the conductivity of dielectric SnO₂ particles coated with a silver layer (8 vol. %) using thermal treatment of a precursor, *viz.*, an Ag(I)-containing polymer, is substantially increased ($\sigma = 1 \times 10^{-3}$ S m⁻¹), whereas $\sigma = 2 \times 10^{-7}$ S m⁻¹ for a mechanical mixture of SnO₂ and Ag powders (16 vol. %).⁵³⁶

Particular attention has been given to multicomponent metal-containing hybrid nanocomposites, which find use in the production of electrode materials for galvanic cells,⁵³⁷ high-T_c superconducting ceramics, *etc.* Materials prepared by the sol-gel method are used as piezoelectric ceramic fillers in acoustic converters as well as in the medical diagnostics. Thus coatings with dense homogeneous microstructures possessing the enhanced mechanical strength and improved piezoelectric characteristics were formed by sheet rolling (413 K, 20–30 MPa) of polymer–ceramic mixtures of polyvinylidene fluoride with PbTiO₃ (up to 65 vol. %).⁵³⁸

The preparation of modifying thin (3–7 nm) magnetic coatings by electrochemical methods has considerable promise. In particular, organosilanes are coated with a film containing α -Fe (70 at. % of Fe), magnetite Fe_3O_4 and an admixture of Fe_2O_3 .⁵³⁹

Sometimes magnetically active particles are introduced into different gels, *viz.*, into silicon,⁵⁴⁰ polyacrylamide,⁵⁴¹ poly(ethylene oxide)⁵⁴² *etc.* gels.⁵⁴³

To improve the electrophysical and magnetic characteristics of nanocomposites, ferroplastics are often formed in magnetic fields. In this case, magnetic orientation occurs. Thus neodymium ferrite is prepared in fields with the intensity of 3×10^{-4} – 3×10^{-3} T and then it is subjected to the mechanochemical action (pressing,⁵⁴¹ treatment between Bridgman's anvils⁵⁴³ or a combination of these procedures⁵⁴⁴). This makes it possible to produce magnetically filled matrices with oriented chain structures, which are used in the techniques for the production of varnishes and films and are of considerable interest as elements of systems for data recording. The formation of coatings under conditions of hardening in a variable magnetic field makes it possible to prevent precipitation of nanoparticles, which are either concentrated closer to the film surface or uniformly distributed throughout the body of the film. These materials are used as drug carriers as well as for the magnetic recording of data, magneto-separation and the preparation of composites possessing the magneto-optical properties and magnetic liquids (for example, oligoorganosiloxanes). Organometallic ferromagnetics based on polymetalloorganosiloxanes possess peculiar magnetic properties.^{545, 546}

Hybrid polymer-inorganic nanocomposites are characterised by a unique combination of the optical and semiconducting properties associated with the sensitivity of plasmon vibrations (the frequency, the intensity, the shape and the width of the band) not only to the nature of the matrix and the morphology of the nanocomposite but also to the particle size. The character of interactions between the electronic and atomic subsystems changes substantially as the linear sizes of semiconductor particles decrease to values comparable with the electron wavelengths, which is manifested in the quantum dimensional effects, *viz.*, in nonlinear optical effects, doubling of the frequency of the incident radiation (generation of the second harmonic), the 'blue shift' of the exciton absorption band, *etc.* The ability of these nanocomposites to form films and the ease of their treatment make it possible to use them for the preparation of dispersing optical elements, band-pass light filters and other high-quality thin-filmed coatings (only ~ 5 – 20 nm thick), which are used in the optoelectronics. For example, the production of modern integrated circuits is based on the so-called planar technology combining processes of the nanolithography (the formation of nanosized surface figures as lines and dots) and the etching. With the aim of decreasing the sizes of elements of optoelectronic integrated circuits to < 100 nm, new techniques of the lithography (in particular, electron-ray, ion-beam and X-ray) as well as new procedures for the dry etching (plasma-chemical, reactive ionic, *etc.*) are used.

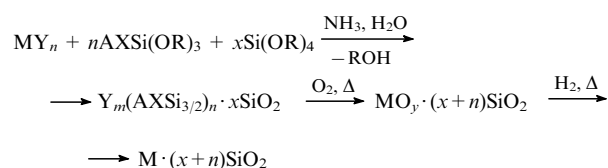
Almost all materials of this kind are characterised by a nonlinearity of the optical properties manifested in a substantial strengthening of the local field of the light wave. The latter is quantitatively characterised by the third-order susceptibility, the nonlinear indices of refraction and the nonlinear absorption coefficient. These effects are widely used in spectroscopic practice (local nonperturbing methods of diagnostics, electron-optical image converters, *etc.*). This is particularly true of sol-gel glasses based on CdS, nanohybrid composites based on polymers and SiO_2 (or V_2O_5), Langmuir–Blodgett films, *etc.*⁵⁴⁷ If the sizes of semiconducting nanosized particles in matrices are much smaller than the wavelength of the exciting field ($\ll \lambda/20$), the nonlinear optical properties manifest themselves in the fact that 'quantum points' appear in nanocomposites (quantum-point polymers).^{548–550} There is a definite relationship between the wavelength of the exciting radiation and the sizes of nanoparticles.

Nanocomposites of this type can be used as active layers of light-emitting diodes.⁵⁵¹

In the previous sections, procedures for the insertion of transition metal ions into polymers in the stage of the sol-gel synthesis or intercalation have already been mentioned. The materials thus obtained serve, for example, for the preparation of coloured light guides, which have a broad spectrum of applications, *viz.*, from storage elements to highly sensitive detectors.

Let us consider the use of hybrid nanocomposites in catalytic, most often hydrogenation, processes. Under conditions of formation of catalysts and hydrogen adsorption, dislocations are fixed at interblock boundaries of polymer-stabilised nanoparticles. These particles have highly active surfaces and developed internal structures. A polymeric matrix hinders smoothing of numerous defects upon catalyst ageing. Of prime importance in the catalysis is a knowledge of the surface composition and S_{spec} and the possibility to control these parameters. The inherent size of nanosized particles is comparable with the molecular sizes of the compound subjected to catalytic conversion. This fact is responsible for the characteristic features of the kinetics and the mechanism of the reactions with the participation of nanosized particles. In particular, the high efficiency of colloid-metallic catalysts in multiple-electron processes results from the fact that these catalysts are 'reservoirs,' which can readily incorporate electrons.

Polymer-stabilised metal nanoparticles are primarily of theoretical interest as excellent models for studying the influence of the dimensional effects on the catalytic activity. Using these particles as examples, many concepts of the fundamental theories of catalysis can be verified. In addition, since nanocomposites are involved both in homogeneous and heterogeneous catalytic processes, they provide an additional possibility of revealing the relationships between homogeneous, heterogeneous and enzyme catalysis.⁵⁵² In a number of characteristics, these nanocomposites are similar to homogeneous catalysts although they also inherit the principal features of heterogeneous contacts. Thus huge Pd_{561} clusters can be considered as a bridge between homogeneous and heterogeneous catalysts.⁵⁵³ Composites based on nanosized particles of platinum and other metals, which are incorporated into glassy carbon matrices, can be assigned to the same type of catalysts.⁵⁵⁴ Of particular interest are catalysts based on organic–inorganic hybrid materials in which catalytically active metals incorporated into an oxide network are dispersed. For example, highly dispersed heterogeneous catalysts in a SiO_2 network prepared from substituted alkoxysilanes are known (see the review⁵⁵⁵).



Protective polymeric coating prevents poisoning of a metallopolymeric catalyst by potential catalytic poisons of the dibenzothiophene type.

Nanocomposites exhibit the high catalytic activity in elimination of hydrogen under the action of visible light⁵⁵⁶ [for example, the ethylenediaminetetraacetate (electron donor)– $\text{Ru}^{2+}(\text{bipy})_3$ (photocatalyst)–methyl viologen (electron acceptor) system]. Substantial success has been achieved in charge separation as well as in the design of efficient photocatalysts with the use of semiconducting nanomaterials (primarily, based on TiO_2) prepared by the sol-gel method (see the reviews^{557, 558}). The additional introduction of transition metal ions (for example, of copper^{559, 560}) in the stage of formation of these materials substantially enhances the efficiency of the photocatalytic reaction. These systems exhibit high activity also in low-temperature oxidation of CO .^{561, 562}

The use of polymer-protected nanoparticles can contribute new specific features to catalysis. A platinum sol as well as Pt on Al_2O_3 are the well-known enantioselective catalysts of hydrogenation processes.⁵⁶³ The potential possibilities of the use of hybrid nanocomposites in catalysis are far from all realised.⁵⁶⁴

IX. Conclusion

To summarise, a great diversity of aspects of the chemistry of nanocomposites is progressing extensively. In the coming years, procedures for the synthesis of multicomponent materials based on ecologically pure solid-state reactions will be developed. Apparently, the use of alcoholates or oxoalcoholates of nontraditional metals, for example,⁵⁶⁵ of Ta^{5+} or Nb^{5+} , in sol-gel procedures will have promise. This refers equally to new intercalation systems. Procedures for the preparation of hybrid materials of the 'network-in-network' type will be studied in more detail. The mechanism of their phase separation and the structures of the resulting nanocomposites will be elucidated. These materials will be formed with the use of monomers, which are traditionally used for the preparation of network polymers, including interpenetrating networks. A search for the optimum modes of formation of new types of lattices ('host' and 'guest' components in intercalated nanocomposites) is still in progress and studies of intracrystalline 'host-guest' interactions and their effect on the electronic properties of complex systems are being continued. For this purpose, it is necessary to reveal principal mechanisms of the orientation effect of pores and interlayer formations on the crystallinity and the stereoregularity of the polymer formed, which is one of the fundamental problems of physical chemistry of polymers and composite materials by itself. The approaches to the preparation of organic-inorganic nanocomposites surveyed in this review may be useful in the synthesis of different single-phase crystalline nanometal-ceramic products with complex compositions, for example, the MgM_2O_4 - α - Al_2O_3 systems ($\text{M} = \text{Al}$ or Cr) (< 10 nm). These products can also be synthesised with the use of Grignard reagents. Theoretical studies of the nature of bonds between metals (Fe, Ni, Cu and Ag) and the surface oxygen anion in cluster models started by Johnson and Pepper⁵⁶⁶ will help in the understanding of the structures of these materials. The use of LBF, which incorporate isolated cluster molecules or nanosized particles, in molecular electronics may have considerable promise. Finally, the nanophase materials technology requires the appropriate scientific support, i.e., the construction of new instruments as well as the development of techniques for working with nanosized materials.

The generality of many processes occurring both in the living and nonliving nature can give impetus to studies of nanobiocomposites. In this review, a reasonably fair, though incomplete, picture of applications of nanobiocomposites to studies of organised matter and the preparation of hybrid bioceramic nanomaterials is given.

The statements that the science and engineering will be developed on the nanosized level in the XXI century seem to be realistic because nanometer sizes of individual elements (for example, densities of the arrangement of microelectronic elements on crystal surfaces) are attained in many traditional technologies.

The structure-property relationship is the fundamental problem of modern chemistry and physics of hybrid nanocomposites. A great deal needs to be done before this problem is solved.

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Thermal transformations of organic compounds of divalent sulfur

M G Voronkov, E N Deryagina

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Abstract. Published data on thermolysis of organic compounds of divalent sulfur and on thermal synthesis involving these compounds are summarised. The bibliography includes 201 references.

I. Introduction

Among the great variety of the ways of formation and chemical transformations of organic compounds of divalent sulfur, the thermal reactions, *i.e.*, the processes which occur at elevated temperatures in the absence of catalysts or promoters, take a special place. Such reactions proceeding in the earth's crust over millions of years have led to the formation of sulfur-bearing components of combustible fossils.

Mankind has dealt with the thermal reactions of sulfurous compounds from time immemorial, whenever a sulfur-containing material of organic origin is subjected to thermal treatment.

All combustible fossils, *viz.*, oil, bituminous and brown coals, oil-shales and natural gas, contain some amount of sulfur compounds. Therefore, high-temperature reactions of formation and thermal transformations of organosulfur compounds accompany virtually all processes of thermal fossil treatment. These are, for instance, the distillation and cracking of high-boiling oil fractions at temperatures from 300 to 800 °C and dry-distillation of bituminous and brown coals, oil-shales and peat at 450–1000 °C.

Thermal reactions of organosulfur compounds were studied in the very early stages of the development of chemistry as a science. However, the detailed exploration of these processes was started only in the past century.

The interest in thermal reactions of particular sulfur-containing organic compounds and in high-temperature syntheses involving these compounds is caused by the necessity to solve a number of problems, the most important of which are listed below.

1. The utilisation of sulfur-containing wastes in oil-refining, gas-, coal- and pulp-processing industries.

2. The development of thermal methods for the synthesis of organic and organosulfur compounds which are difficult to obtain alternatively.

3. Mechanistic studies of free-radical thermal reactions of sulfur-containing organic compounds occurring with involvement of free radicals. The development of methods for the generation of thiyl radicals, the evaluation of their reactivities and possible utilisation in high-temperature synthesis.

4. The generation of labile sulfur-containing intermediates, *e.g.*, thioformaldehyde, ethylenethiol, thioketones, sulfines, sulfenes, sulfenic acids, dialkylsilanethiols, *etc.*, using the flash pyrolysis technique and the development of methods for the detection of such intermediates.

The present review is devoted to the thermal transformations of organic compounds of divalent sulfur, except for thiones, and to the latest achievements in the field of high-temperature synthesis involving these compounds. Earlier, only a few papers^{1,2} with a brief survey of the literature on these issues have been published.

II. Thiols

1. Alkanethiols

Pyrolysis of alkanethiols in the gas phase at temperatures above 425 °C yields hydrogen sulfide and alkenes as the major products.^{3,4} The degree of decomposition of alkanethiols increases with an increase in the reaction time and temperature.⁵ Aliphatic hydrocarbons do not react with alkanethiols or products of their decomposition. Benzene accelerates thermolysis of alkanethiols, whereas carbon dioxide or hydrogen inhibit this process. Higher homologues of alkanethiols are somewhat less stable than the lower ones. Linear alkanethiols are more stable than their branched isomers,⁶ especially at higher temperatures (475 °C).

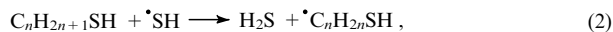
Hydrogen sulfide, hydrogen and methane are the pyrolysis products of methanethiol.⁵ Dialkyl sulfides, thiophene, hydrogen sulfide and elementary sulfur have been found among the thermolysis products of other alkanethiols.⁴ The decomposition is catalysed by metal sulfides and inhibited by cyclohexene.⁷ Since in both cases the ratio of the surface to the volume of a reactor does not affect the reaction rate,⁸ a free-radical chain mechanism for the thermolysis of alkanethiols has been suggested.^{6,9}



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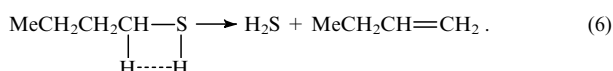
Uspekhi Khimii 69 (1) 90–104 (2000); translated by S V Chapyshev



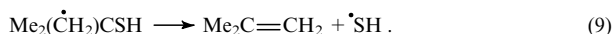
The main process is accompanied by parallel reactions (4) and (5).



The thermal decomposition of *n*- and *sec*-butanethiols in a flow system follows a molecular mechanism involving the synchronous abstraction of hydrogen from the α -carbon atom *via* a cyclic transition state.¹⁰



The decomposition of 1,1-dimethylethanethiol under the same conditions follows a free-radical mechanism.⁹



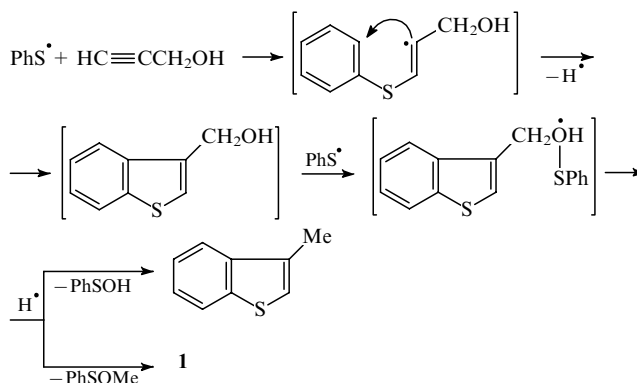
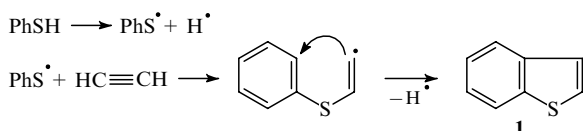
The activation energy for reaction (8) was found to be 7 kcal mol⁻¹. The pyrolysis of isomeric butanethiols in a static system occurs as a homolytic process in accordance with Eqns (1)–(8).⁸ The thermal decomposition of cyclohexanethiol at 420–470 °C and under reduced pressure leads to the formation of hydrogen sulfide and cyclohexene.¹¹ Hydrogen sulfide accelerates this process, while cyclohexene retards it. In the presence of sulfur dioxide or over activated carbon at 425 °C, cyclohexanethiol is converted into benzenethiol.¹² α -Toluenethiol decomposes more readily than the lower alkanethiols yielding hydrogen sulfide and 1,2-diphenylethane.^{4–6} Ethanethiol is converted into thiirane and hydrogen sulfide on heating *in vacuo*.¹³

Most of the data available suggest a free-radical mechanism of alkanethiol decomposition, the initial step of which involves the cleavage of the C–S bond and generation of an $\cdot\text{SH}$ radical. The activation energy of this reaction presumably equals the energy of the C–S bond dissociation. Owing to the generation of thiyl radicals, high-temperature reactions of alkanethiols with aryl halides can take place yielding the corresponding arenethiols.¹⁴

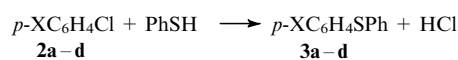
2. Arenethiols

Decomposition of benzenethiol begins at about 200 °C.¹⁵ At 530–600 °C, benzenethiol, its derivatives and naphthalenethiol are converted into the corresponding diaryl sulfides.¹⁶ These reactions are catalysed by copper sulfide, cadmium sulfide and activated carbon; in the presence of these catalysts conversions occur at lower temperatures (300–500 °C).^{17,18} The *cis*–*trans* isomerisation of the C_{Ar}S–H bond takes place on flash vacuum pyrolysis of benzenethiols at 70–600 °C.¹⁹ Under reduced pressure of ozone, benzenethiol decomposes at 30–125 °C to form oxygen, carbon dioxide, sulfur dioxide and polymeric products depositing on the reactor walls.²⁰

Benzenethiol reacts with acetylene at 550–590 °C to give benzo[b]thiophene. A similar reaction with propargyl alcohol at 450–630 °C yields benzo[b]thiophene (**1**) and 3-methylbenzo[b]thiophene. It is supposed that pyrolysis of benzenethiol involves the generation of thiyl radicals, which add to the triple bonds of the substrates.²¹

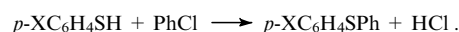


Gas-phase reactions of benzenethiol with chlorobenzene and its *para*-substituted derivatives **2a–d** at 500–600 °C lead to symmetrical (**3a**) and unsymmetrical diaryl sulfides (**3b–d**).^{22,23}



X = H (**a**), Me (**b**), OMe (**c**), Cl (**d**).

Analogous diaryl sulfides are formed in the gas-phase reactions of *para*-substituted arenethiols with chlorobenzene at 500–620 °C.

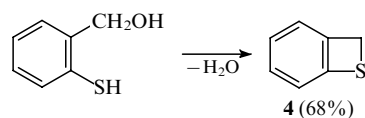


The Arrhenius rate constants for these reactions have been determined.^{23,24}

$\bar{n}$	k / litre mol ⁻¹ s ⁻¹
H	$3.89 \times 10^{10} \exp(-149.90/RT)$
Me	$3.48 \times 10^9 \exp(-140.20/RT)$
OMe	$4.20 \times 10^8 \exp(-116.57/RT)$
Cl	$7.76 \times 10^{13} \exp(-206.1/RT)$

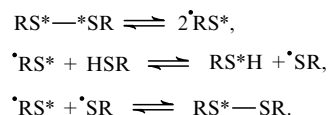
Benzenethiol reacts in the gas phase at 400–530 °C with 1,2-dichloroethene (a 3 : 1 mixture of *E*- and *Z*-isomers) to give β -chlorovinyl phenyl sulfide (a 1 : 1 mixture of *E*- and *Z*-isomers) in 84% yield.²⁵ The reaction of benzenethiol with β -bromostyrene in the liquid phase at 140–160 °C leads to phenyl β -styryl sulfide.²⁶ At 125–215 °C, benzenethiol readily reacts with 2- and 4-bromophenols, 1-bromo-2-naphthol, 1-bromonaphthalene and 1-bromoanthracene to form the corresponding aryl phenyl sulfides.²⁷

o-Chlorobenzenethiol and *o*-chloromethylbenzenethiol eliminate hydrogen chloride on flash vacuum pyrolysis.¹⁹ At 700 °C in vacuum, hydroxymethylbenzenethiol is converted into benzothiethene (**4**).²⁸

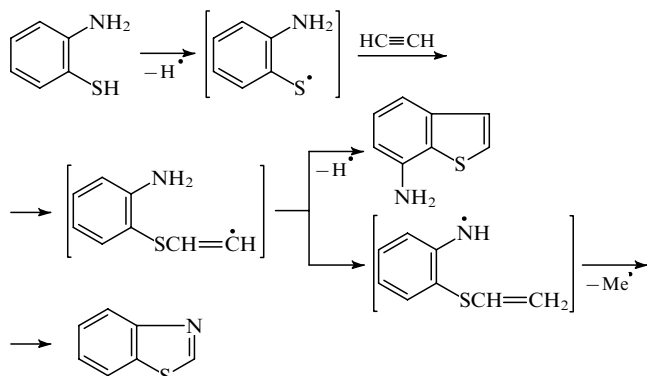


When a mixture of toluenethiol and ³⁵S-labelled ditolyl disulfide is heated, isotope exchange between thiyl radicals occurs. This process is accelerated by UV irradiation (Scheme 1). The reaction rate does not depend on the thiol concentration and is determined by the proneness of a disulfide to generate thiyl radicals as a result of S–S bond cleavage.²⁹

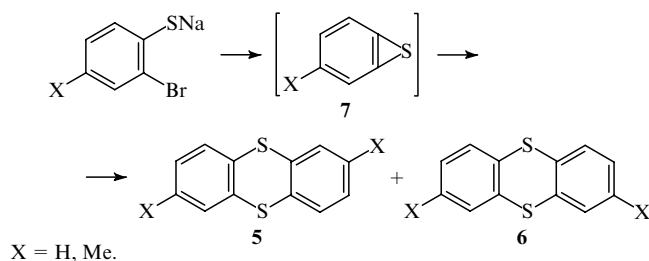
Scheme 1



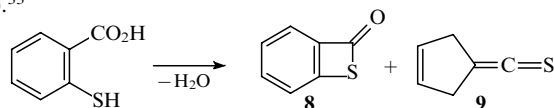
7-Aminobenzo[*b*]thiophene and benzothiazole are the major products in the gas-phase reaction of 2-aminobenzenethiol with acetylene at 450–600 °C. The maximum yields of these products (39% and 41%, respectively) are achieved at 600 °C.³⁰



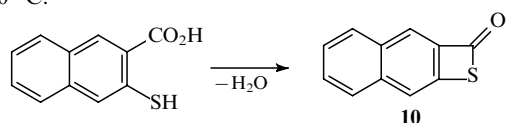
Pyrolysis of sodium 2-bromobenzenethiolate or its derivatives results in thianthrene or a 1:1 mixture of the corresponding isomeric thianthrenes **5** and **6**, thus suggesting the intermediate generation of short-lived thiirene **7**.^{31,32}



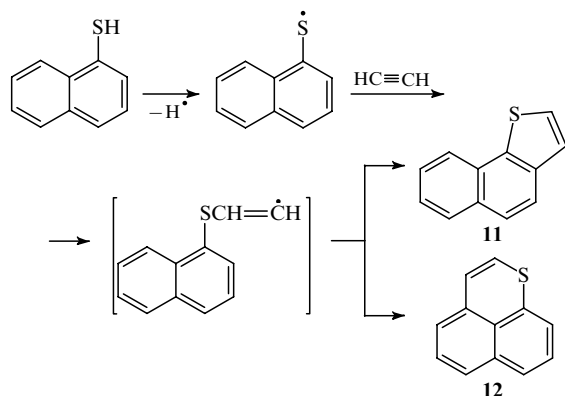
Flash vacuum pyrolysis of 2-mercaptobenzoic acid at 610 °C gives rise to benzothiet-2-one (**8**) and 1,4-dihydrofulvenethione (**9**).³³



Similarly, 3-mercapto-2-naphthoic acid is converted into naphtho[2,3-*b*]thiet-2-one (**10**) on flash vacuum pyrolysis at 840 °C.³⁴

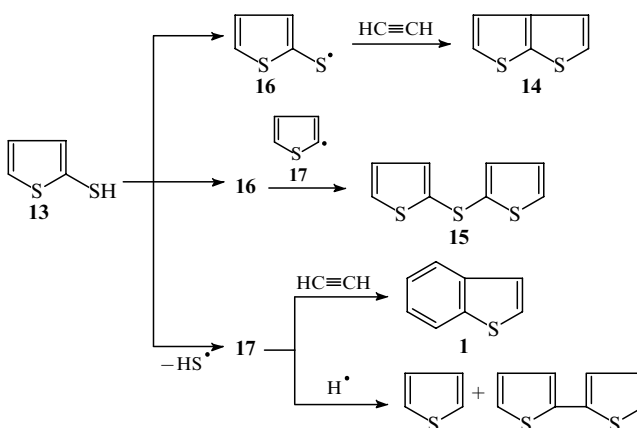


Naphthalene-1-thiol reacts with acetylene at 410–700 °C to form naphtho[1,2-*b*]thiophene (**11**) and 1-thiaphenylene (**12**) in 47% and 60% maximum yields, respectively.³⁵

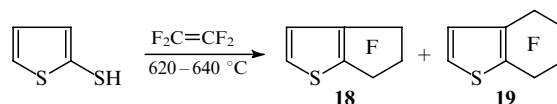


3. Hetarenethiols

The gas-phase reaction of 2-thiophenethiol (**13**) with acetylene at 500–600 °C affords thieno[2,3-*b*]thiophene (**14**) together with bis(2-thienyl) sulfide (**15**), thiophene and benzo[*b*]thiophene.³⁶ The complex character of transformations of 2-thiophenethiol is caused by the initial cleavage of the S–H and C–S bonds and the generation of radicals **16** and **17**, which either react with acetylene or recombine.



4,4,5,5,6,6-Hexafluorocyclopenta[*b*]thiophene (**18**) is the main co-pyrolysis product of 2-thiophenethiol with tetrafluoroethylene at 620–640 °C; 4,4,5,5,6,6,7,7-octafluorocyclohexa[*b*]thiophene (**19**) is also formed.³⁷



The reaction mechanism involves the generation of difluorocarbene from tetrafluoroethylene, the replacement of the thiol group in 2-thiophenethiol by this carbene and the subsequent addition of the C-centered radical thus formed to tetrafluoroethylene. The product **19** is formed due to the elimination of the SH group from the parent thiol and the reaction of thienyl radical with tetrafluoroethylene.

Bromothiophenethiols are unstable and decompose on distillation with elimination of hydrogen bromide and hydrogen sulfide.³⁸

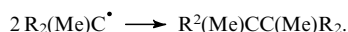
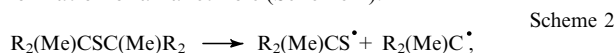
III. Sulfides

Thermal decomposition of organic sulfides usually involves cleavage of the C–S bonds. The strength of this bond is different in different compounds. In dialkyl sulfides, either only the *3p*-orbitals³⁹ or the hybrid *sp*- and *spd*-orbitals^{40,41} are involved in the formation of the C–S σ -bond. The sulfur atom in sulfides can exhibit both electron-donating and electron-withdrawing properties. The latter is true when electron-withdrawing substituents are present in the α -positions to the sulfur atom. In the absence of such substituents the electron-withdrawing properties of the sulfur atom are not so pronounced, since its *3d*-orbitals in the ground state are diffuse and the energy of their occupation by an electron cannot be compensated by the energy of covalent bond formation. The presence of electron-withdrawing substituents in sulfides favours the localisation of a positive charge on the sulfur atom, thus weakening the C–S bond. The lone electron pairs of the sulfur atoms in sulfides can conjugate with the π -system of a multiple bond or an aromatic ring (contribution of the structures with the $2p\pi$ – $3p\pi$ bond). Owing to this effect, vinyl and aryl sulfides are rather weak electron donors and are characterised by high strengths of their C–S bonds.

1. Dialkyl sulfides and their derivatives

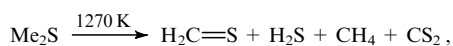
Studies on the pyrolysis of dialkyl sulfides were begun in 1928 with the aim of elucidation of the course of transformations of sulfur-containing components of raw oil and oil products upon refining.⁴² It was found that diethyl sulfide decomposes at 500 °C to form considerable amounts of hydrogen sulfide, gaseous hydrocarbons (38 mass %) and ethanethiol (10 mass %).^{42, 43} Diisopentyl sulfide is much more stable. The products of its pyrolysis at 500 °C contain mostly the recovered diisopentyl sulfide, 3-methylbutane-1-thiol and thiophene derivatives. Among the gaseous products, alkanes (64%), alkenes (30%), hydrogen sulfide and hydrogen (0.5%) have been found. Dibutyl sulfide decomposes at 500 °C rather rapidly to form hydrogen sulfide and thiols; the thermolysis is accelerated in the presence of benzene and decelerated in the presence of n-heptane. In a vacuum, dibutyl sulfide decomposes at 380–410 °C yielding ethylene and polysulfides.⁴⁴ Isobutylene, hydrogen sulfide, isobutane, 1,1-dimethylethanethiol and sulfur are the pyrolysis products of di(*tert*-butyl) sulfide in a static system at 25–250 Torr and 360–413 °C. In the presence of cyclohexane, the yield of the thiol is sharply increased, while the yield of hydrogen sulfide is diminished several-fold and sulfur is not formed at all. In a flow system at 446–466 °C, small amounts of ethane, ethylene, propane, propylene and butene are also formed.⁴⁵ Thermal stabilities of most dialkyl sulfides both in pure form and in solutions of Surakhansk kerosene (fraction with b.p. 180–200 °C) have been determined.⁴⁶

The decomposition of dialkyl sulfides in the gas phase at 400–800 °C to yield hydrogen sulfide and the corresponding alkenes follows a free-radical mechanism involving the intermediate formation of alkanethiols (Scheme 2).^{42, 47–49}



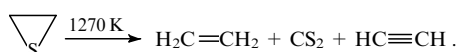
If the pyrolysis of alkanethiols is carried out in vacuum (0.1 Torr), the yield of hydrogen sulfide is quantitative. Both unsymmetrical dialkyl sulfides and those with branched aliphatic chains are less thermally stable than symmetrical di(*n*-alkyl) sulfides.

Dialkyl sulfides bearing methyl groups in the β -position are converted into the corresponding alkenes and hydrogen sulfide on flash vacuum pyrolysis at about 1000 K.

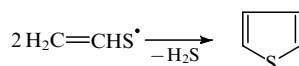
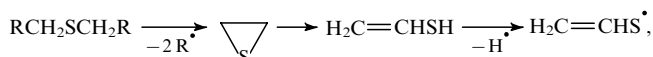


All derivatives with an α -methyl group and thiirane are more thermally stable and decompose at higher temperatures.⁵⁰

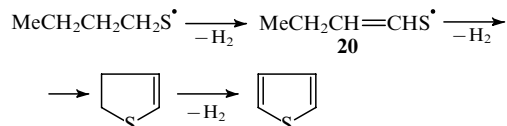
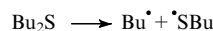
Thiirane is the most stable sulfide despite the strain in its molecule. It forms ethylene, acetylene and hydrogen sulfide at 1270 K.⁵⁰



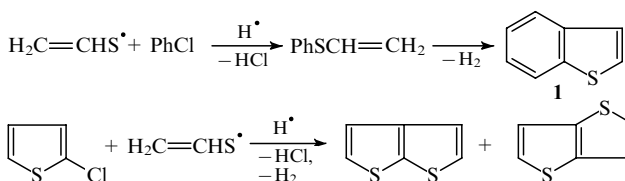
A new reaction pathway in the thermal decomposition of di(*n*-alkyl) sulfide leading to ethylenethiol and its further conversion into thiophene was found later.^{51, 52} Most likely, ethylenethiol is generated from dimethyl sulfide and other dialkyl sulfides according to a scheme common for all dialkyl sulfides through the initial formation of thiirane and its subsequent isomerisation.



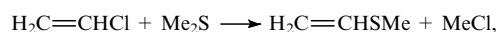
Thiophene is formed from butyl sulfide mostly as the result of an intramolecular cyclisation of the butenethiyl radical **20**.



The gas-phase reactions of dialkyl sulfides with chlorobenzene or 2-chlorothiophene lead to benzo[*b*]thiophene (**1**) and thienothiophenes, respectively.^{52–55}



The reaction of dimethyl sulfide with vinyl chloride in the gas phase at 430–450 °C is accompanied by the formation of 1,1-bis(methylthio)ethane in 30% yield.⁵⁶



Thermolysis of aliphatic sulfides in non-polar solvents (heptane, nonane, octane, decalin) under pressure occurs at 140–250 °C. In these reactions, sulfides and thiols can exchange their RS groups in accordance with the Scheme 1. Highest sulfides and lowest thiols have higher exchange rates.^{48, 57}

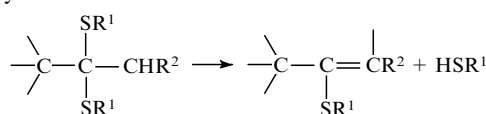
Decomposition of aliphatic sulfides at 300–400 °C in melts of ZnCl₂–HCl, ZnCl₂–LiCl, ZnCl₂–SnCl₂, SnCl₂–KCl, ZnCl₂–KCl–NaCl, CuCl–KCl–NaCl eutectics leads to a mixture of alkanes, C₂–C₄ alkenes and hydrogen. Complexes of the (Pr₃S)₃(ZnCl₂)₂ type are formed as intermediate products. In zinc-containing eutectics, sulfides decompose faster to form predominantly alkenes the structures of which correspond to those of the alkyl chains in the starting sulfides. Sulfur is liberated as ZnS, which is then dissolved in the melt.⁵⁸

Thermal decomposition of benzyl methyl sulfide and substituted 1,2-bis(benzylthio)ethanes proceeds according to the Scheme 2.^{5, 59}

Polyethylene sulfide decomposes at 230 °C to form hydrogen sulfide, ethane and a small amount of ethanethiol. The activation energy for this reaction corresponds to the energy of a homolytic cleavage of the C–S bond in macromolecular chains of polyethylene sulfide.⁶⁰

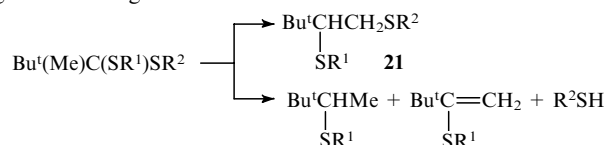
Thermolysis of bis(2-ethoxyethyl) sulfide, 1,1-bis(ethylthio)ethane and 1,3-bis(propylthio)propane involves the initial cleavage of the C–S bonds and occurs in accordance with reactions (1)–(4). The dissociation energies of the C–S bonds in these compounds have been calculated.⁶¹

Heating of dialkyl dithioacetals to 130 °C results in the elimination of a thiol and the formation of the corresponding vinyl sulfide.^{62–64}

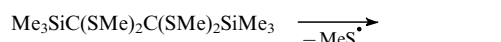
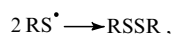
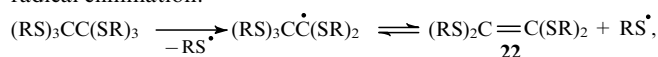


R¹ = Alk, Ar; R² = Alk.

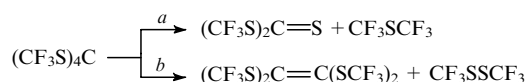
The main process is accompanied by the 1,2-migration of the thiyl group and the formation of the saturated sulfide **21** according the following scheme.^{65–68}



Hexakis(alkylthio)- and tetrakis(methylthio)bis(trimethylsilyl)ethanes undergo thermolysis at 110 °C to form the corresponding ethylene derivatives **22** as the result of the alkylthiyl radical elimination.⁶⁹



Vacuum pyrolysis of tetrakis(trifluoromethylthio)methane at 400 °C and 1–1.5 Torr leads mainly to bis(trifluoromethyl) trithiocarbonate together with small amounts of bis(trifluoromethyl) sulfide, bis(trifluoromethyl) disulfide and tetrakis(trifluoromethylthio)ethylene. The latter is formed as the major product on pyrolysis of tetrakis(trifluoromethylthio)methane at 400 °C under atmospheric pressure. The reaction mechanism involves the formation of free radicals and carbenes.⁷⁰



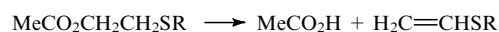
(a) 400 °C, 1 Torr; (b) 400 °C, 760 Torr.

Hexakis(trifluoromethylthio)ethane undergoes the C–C bond dissociation producing tris(trifluoromethylthio)methyl radicals even at 30 °C.⁷¹

2-Chloroethyl methyl sulfide eliminates hydrogen chloride at 360–400 °C.⁷² The rate of its decomposition at 400 °C is 234-fold higher than that for ethyl chloride or ethylene chlorohydrin.⁷²

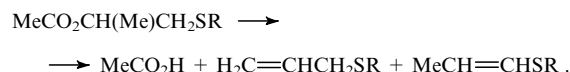


2-Alkylthioethyl acetates eliminate acetic acid at 460–465 °C to form the corresponding alkyl vinyl sulfides.⁷³



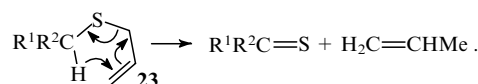
R = Me, Buⁿ, Bu^t, Bn.

2-Alkylthio-1-methylethyl acetates are converted into a mixture of 1- and 3-(alkylthio)propenes at 500 °C. 3-Isomers are predominant at 400 °C and short contact times.⁷⁴



Gas-phase thermolysis of alkyl and cycloalkyl allyl sulfides at 400–500 °C is accompanied by a molecular rearrangement involving either four- or six-membered cyclic transition states and leading to the corresponding alkenes and thioaldehyde.⁷⁵

Upon flash pyrolysis at 600–650 °C, allyl sulfides **23** eliminate propene and are converted into the corresponding thiocarbonyl compounds.^{76,77}

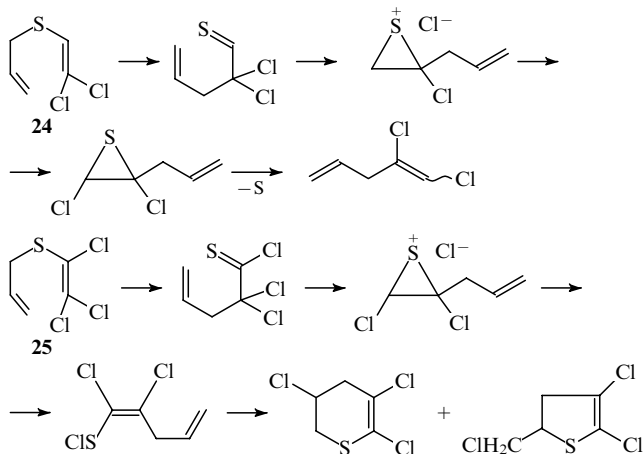


Thioacrolein and thiobenzaldehyde have been found in the pyrolysis products of diallyl and allyl benzyl sulfides.^{76,78} 1,3-Bis(allylthio)propane decomposes at 520 °C to form unstable compounds which are rapidly converted into a polymer built of –S(CH₂)₃S– units.⁷⁹ The extent of isomerisation of a *cis*-rotamer of methyl vinyl sulfide into the *gauche*-rotamer at 200–600 °C is 20%.⁸⁰

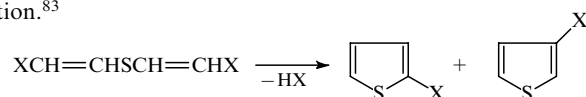
2. Vinyl and ethynyl sulfides

Thermolysis of *tert*-butyl 1-propenyl sulfide at 340–390 °C proceeds tenfold faster than that of di(*tert*-butyl) sulfide and is not inhibited by cyclohexene. Isobutene, isobutane and propenylthiyl trimer are the reaction products.⁴⁵

Heating of allyl 2,2-dichlorovinyl sulfide (**24**) at 160–180 °C and of allyl 1,2,2-trichlorovinyl sulfide (**25**) at 100–120 °C results in unusual rearrangements leading to 1,2-dichloropenta-1,4-diene and a mixture of 2,3-dichloro-5-chloromethyl-4,5-dihydrothiophene and 3,5,6-trichloro-3,4-dihydropyran-2*H*-thione, respectively. The mechanism of the reactions involves a [3,3]-sigmatropic rearrangement and the formation of thiirane intermediates.⁸¹

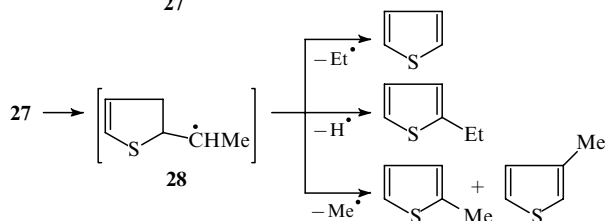
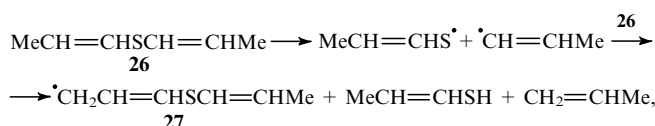


Gas-phase pyrolysis of divinyl sulfide at 450–560 °C gives rise to thiophene in 40% yield.⁸² At 440–460 °C, 2-chlorovinyl sulfide is converted into 2- and 3-chlorothiophene predominantly through the involvement of the *trans*-isomer in this heterocyclisation.⁸³



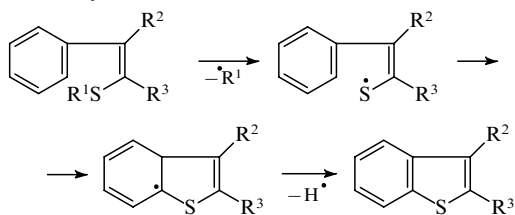
X = H, Cl.

Thermolysis of di(1-propenyl) sulfide (**26**) in the gas phase at 460–540 °C leads to propenethiol, thiophene, methylthiophenes and 2-ethylthiophene. Heterocycles are formed as the result of the intramolecular cyclisation of the sulfide, involving the intermediate formation of radicals **27** and **28**.⁸⁴



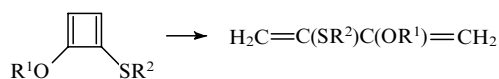
Upon pyrolysis (580 °C) under an atmosphere of nitrogen, alkyl β-styryl sulfides undergo intramolecular heterocyclisation to

give the corresponding benzo[*b*]thiophene derivatives in 50%–70% yields.⁸⁵



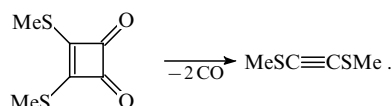
$R^1, R^2, R^3 = \text{Alk, Ph.}$

2-Alkoxy(acyloxy)-3-alkyl(aryl)thiocyclobutadienes are converted into the corresponding dienes on heating to 350 °C as the result of the cleavage of the C(1)–C(4) bond in the rings.⁸⁶

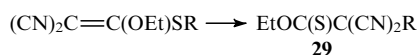


$R^1, R^2 = \text{Me, Ph, CO}_2\text{Me, 4-ClC}_6\text{H}_4, 4\text{-MeOC}_6\text{H}_4, \text{COMe.}$

Pyrolysis of 3,4-bis(methylthio)cyclobutene-1,2-dione at 450 °C leads to the ring opening with the formation of bis(methylthio)acetylene and CO. At 550 °C, hydrogen sulfide and methanethiol are also formed in this reaction.⁸⁷

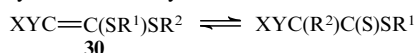


Allyl and propargyl 1,1-dicyano-2-ethoxyvinyl sulfides undergo the Claisen rearrangement on distillation being converted into the corresponding *O*-ethyl thiocarboxylates **29**.⁸⁸



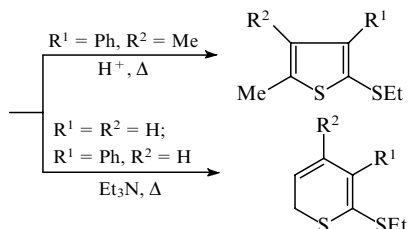
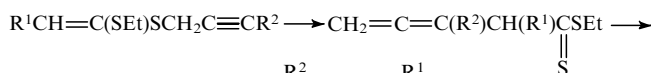
$\text{R} = \text{CH}_2\text{CH}=\text{CH}_2, \text{CH}_2\text{C}\equiv\text{CH.}$

On heating, ketene allyl thioacetals **30** are converted into α -allyl dithiocarboxylates.^{89–91}

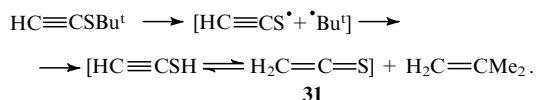


$\text{X, Y} = \text{CO}_2\text{Me, CO}_2\text{Et, CN, Ac, Bz etc.}; \text{R}^1 = \text{Al, Alk}; \text{R}^2 = \text{Al.}$

Ketene allenyl thioacetals undergo the Claisen rearrangement on heating to 80–100 °C to form ethyl acetylenedithiocarboxylates, while ketene ethynyl thioacetals are converted at 100–140 °C into dithiocarboxylates containing the allene fragment.^{92,93} In some cases, the latter undergo partial or complete heterocyclisation on distillation to form 2*H*-thiopyrans or substituted thiophenes.



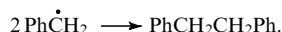
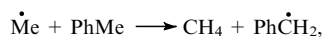
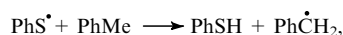
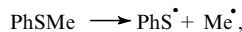
Vacuum pyrolysis of *tert*-butynyl ethynyl sulfide at 500 °C results in the formation of thioketene (**31**), which is more stable than its tautomers, *viz.*, thiirane and ethylthiol.⁹⁴



On heating to 250 °C, dibenzyl sulfide is converted into stilbene with liberation of hydrogen sulfide. The latter partly reduces stilbene to toluene. This produces sulfur which reacts with stilbene to give tetraphenylthiophene.⁹⁵

3. Aryl and hetaryl sulfides

Pyrolysis of a mixture of methyl phenyl sulfide and toluene vapours at 600 °C leads to methane, benzenethiol and dibenzyl. This free-radical reaction was proved to follow a monomolecular mechanism.⁹⁶

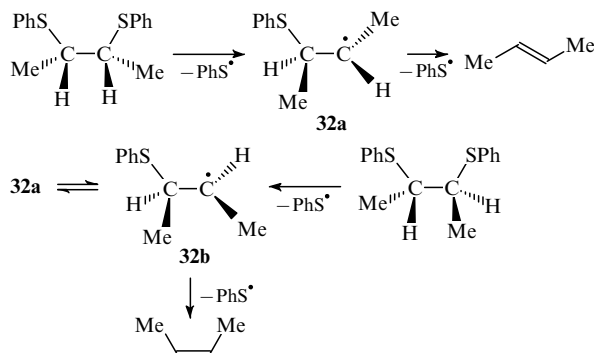


The kinetics of the thermal decomposition of methyl phenyl sulfide and benzyl methyl sulfide at low pressure was studied, and the dissociation energies of the PhS–Me and PhCH₂–SMe bonds were found to be 67.5 and 59.4 kcal mol^{–1}, respectively.⁹⁷ The enthalpies of the formation of radicals MeS[•] and PhS[•] are 34.2 and 56.8 kcal mol^{–1}, respectively.⁹⁷

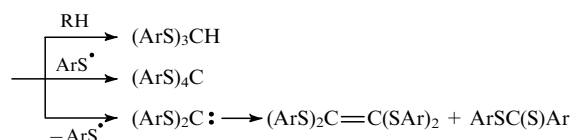
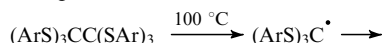
Heating of benzyl phenyl sulfide to 250–270 °C leads to a mixture of liquid and gaseous products, *viz.*, toluene, 1,2-diphenylethane, biphenyl, diphenylmethane, stilbene, benzenethiol, tetraphenylthiophene, benzaldehyde, hydrogen sulfide and carbon dioxide. The yield of benzenethiol reaches 31%.⁹⁸

Flash pyrolysis of benzyl phenyl sulfide in vacuum at 800 °C results in the formation of 1,2-diphenylethane and diphenyl disulfide, which are the recombination products of benzyl and phenethyl radicals, respectively.⁹⁹

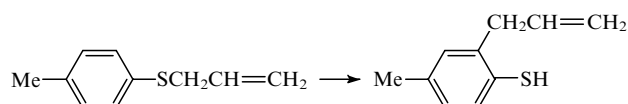
1,2-Bis(phenylthio)ethane and its derivatives decompose at 350 °C to form benzenethiol, diphenyl disulfide and the corresponding alkene. The reaction occurs stereospecifically as a *trans*-elimination. Radicals **32a** and **32b** are converted into the corresponding butenes much more rapidly than they isomerise.¹⁰⁰



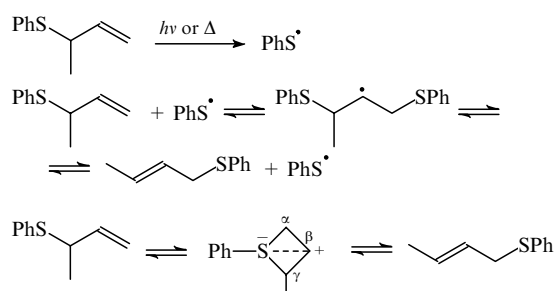
Decomposition of hexakis(phenylthio)ethane begins at 100 °C to generate tris(phenylthio)methyl radicals detectable by EPR spectroscopy.^{101–104} The cleavage of the C–C bond in hexakis(phenylthio)ethane is mostly caused by steric factors (repulsion of the ArS substituents). The disproportionation of the (ArS)₃C[•] radicals is responsible for the formation of the major reaction products.¹⁰¹



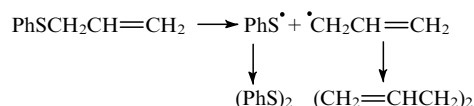
On heating to 200 °C, allyl aryl sulfides undergo the thio-Claisen rearrangement.¹⁰⁵



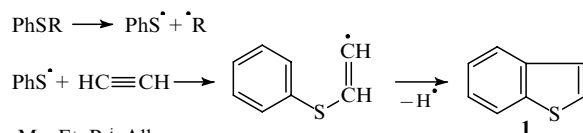
Allyl 2-benzofuryl and allyl 2-benzothieryl sulfides behave similarly on heating. In the latter case, the rearrangement product undergoes further heterocyclisation.^{106, 107} The thioallyl rearrangement usually precedes the thio-Claisen rearrangement in allyl aryl sulfides. Mechanisms involving the intermediacy of free radicals or a four-membered transition state have been considered for these rearrangements.¹⁰⁸



On flash vacuum pyrolysis, allyl phenyl sulfide undergoes initial cleavage of its C—SPh bond resulting in the formation of phenylthiyl and allyl radicals and their subsequent dimerisation.⁵⁰



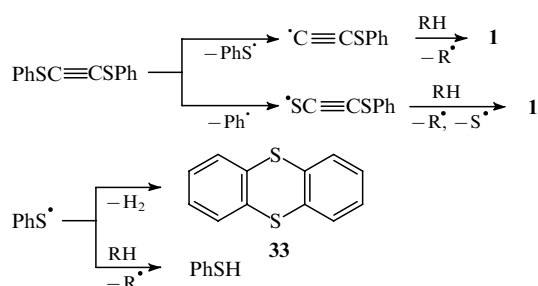
The gas-phase reactions of alkyl phenyl and allyl phenyl sulfides with acetylene at 480–600 °C occur selectively yielding benzo[*b*]thiophene (**1**) as the addition product of phenylthiyl radicals to the triple bond of acetylene.¹⁰⁹



R = Me, Et, Prⁱ, All.

Benzothiophene (**1**) was obtained in the highest yield starting from allyl phenyl sulfide, and this reaction occurs at lower temperature. At 600 °C, vinyl phenyl sulfide undergoes an intramolecular cyclisation to form benzothiophene.¹¹⁰

Pyrolysis of bis(phenylthio)acetylene at 560 °C leads to diphenyl sulfide, benzenethiol, thianthrene (**33**) and benzothiophene (**1**). The reaction involves the generation and subsequent transformations of phenyl and phenylthioethynylthiyl radicals.¹¹¹ In the presence of chlorobenzene, diphenyl sulfide is formed upon its reaction with phenylthiyl radicals.



Diaryl sulfides differ from other diorganyl sulfides in that they possess rather strong C—S bonds. These sulfides are usually stable at 400–600 °C, while at higher temperature they undergo intramolecular cyclisations. Thus at 700–750 °C, diphenyl sulfide, phenyl *o*-tolyl sulfide and 2-hydroxyphenyl phenyl sulfide are

converted into dibenzothiophene, thioxanthene and 4-hydroxy-dibenzothiophene, respectively.¹¹² Dithienyl sulfide is less stable: it decomposes at 500–600 °C to give thiophene, isomeric thiophenethiols and bithienyls and also isomerises into 2,3-dithienyl sulfide. These conversions result from the addition of thiyl radicals to the double bonds of thiophene and to the sulfur atom of sulfides.¹¹³

4. Sulfenyl halides and sulfonium salts

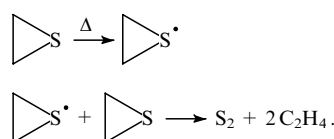
Heating of alkanesulfonyl chlorides to 100 °C affords alkyl chlorides in low yield.¹¹⁴ Flash pyrolysis of methanesulfonyl chloride at 590 °C leads to thioformaldehyde.¹¹⁵ Benzenesulfonyl chloride decomposes at 100 °C to form chlorobenzene, diphenyl disulfide and sulfur monochloride. At 90 °C, 4-methyl- and 4-methoxy-benzenesulfonyl chlorides eliminate sulfur to yield the corresponding *para*-substituted chlorobenzenes.¹¹⁴

Phenyldiarylsulfonium halides undergo complete thermolysis at 250 °C yielding a mixture of aryl halides and diaryl sulfides containing all possible combinations of the aryl substituents in their molecules. A pair 2,5-Me₂C₆H₃X and 4-MeC₆H₄SPh is formed in the highest yield upon pyrolysis of (2,5-dimethylphenyl)(phenyl)(*p*-tolyl)sulfonium chloride.¹¹⁶

5. Cyclic sulfides

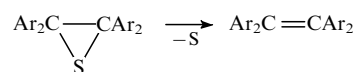
Thiirane (ethylene sulfide) is the simplest three-membered cyclic sulfide with a thermodynamically unfavourable three-centre dipolar atomic system which is, however, stabilised by the efficient involvement of the non-bonding orbitals of the heteroatom into the frontal interactions.¹¹⁷ A characteristic feature of thiirane and its derivatives is their capacity to split the sulfur atom off yielding the corresponding alkene. The conditions required for this reaction, which can sometimes occur at temperatures below 0 °C, depend on the nature of substituents in the thiirane ring. As usual, the substituents exerting the —E-effect and many π -donating systems facilitate the desulfuration.

Thiirane itself decomposes completely in the gas phase at 250 °C into ethylene and elementary sulfur. This is a first-order homolytic reaction the activation energy of which is 40.2 kcal mol^{–1}. Since this value is lower than the enthalpies of the direct elimination of the sulfur atom from the thiirane ring or of the cleavage of this ring, both these processes can be ruled out from mechanistic considerations. A reaction mechanism involving the intermediacy of the excited thiirane has been suggested.^{118, 119}



This mechanism is supported by the complete stereospecificity of the low-temperature thermolysis of *cis*- and *trans*-2,3-dimethylthiiranes.¹¹⁸

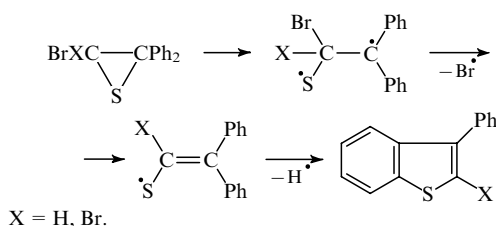
Gas-phase pyrolysis of thiirane at 500–600 °C results in the formation of hydrogen sulfide, ethylenethiol, thiophene, benzo-thiophene and hydrocarbons C₁–C₄ (Ref. 120). Alkyl-, cyclo-alkyl-, 2-aryl- and 2,3-diaryl-thiiranes eliminate sulfur on distillation or moderate heating.^{121–124} Only tetraarylthiiranes decompose at higher temperature (180–215 °C) to form tetraaryl-ethylenes.^{125, 126}



Ar = Ph, 4-MeOC₆H₄, 4-BrC₆H₄, 4-Me₂NC₆H₄ etc.

3,3-Dichloro-2,2-diphenylthiirane undergoes a similar reaction.¹²⁷

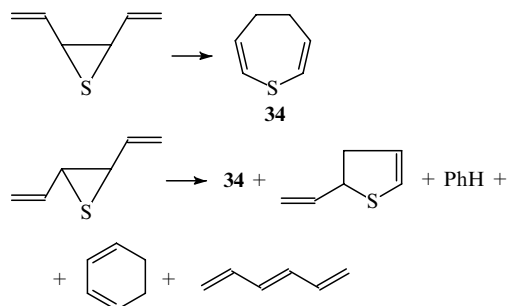
Thermal transformations of 3-bromo- and 3,3-dibromo-2,2-diphenylthiiranes are accompanied by intramolecular cyclisations of the initially generated thiyl radicals without elimination of sulfur.¹²⁷



3-Chloro-2,2-diphenyl-3-X-thiiranes also cyclise into the corresponding benzothiophenes on heating.^{128, 129}

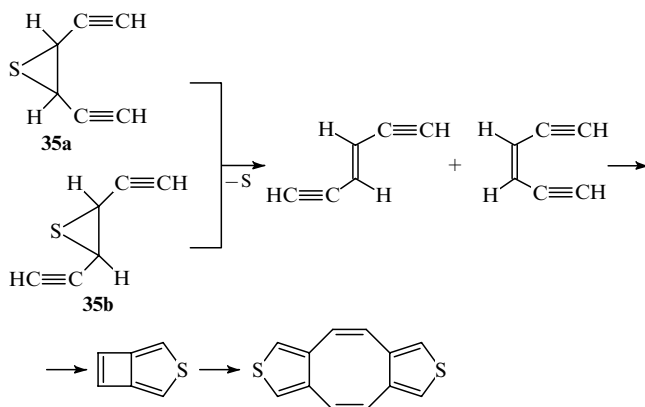
Tetrafluorothiirane is distinguished by its high thermal stability. Its partial conversion into difluorothioformaldehyde, tetrafluoroethylene and a number of other products takes place only at 430 °C.¹³⁰

On thermolysis at 340 °C, *cis*- and *trans*-divinylthiiranes undergo the Cope rearrangement into 4,5-dihydrothiepane (34).¹³¹



Dihydrothiophene, thiophene and *cis*- and *trans*-1-phenylbutadienes are the thermolysis products of *cis*- and *trans*-2-vinyl-3-phenylthiiranes at 360–400 °C.¹³¹ When the concentration of thiirane is relatively high, a bimolecular mechanism predominates.¹³² With a decrease in the concentration of thiirane in the reaction, monomolecular desulfurisation becomes the main process.

Pyrolysis of *cis*- (35a) and *trans*-2,3-diethynylthiiranes (35b) in a solution (toluene-*d*₈, 100 °C) yields only sulfur-free alkenes. If the pyrolysis of *cis*-isomer 35a is carried out in a flow system, thienocyclobutadiene is formed in 6% yield along with alkenes. This diene dimerises on standing in benzene solution.



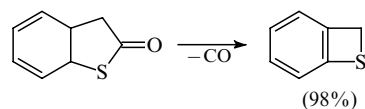
Thus, the data presented here show that in the thermal decomposition of thiirane and its derivatives at temperatures up to 200–350 °C the elimination of sulfur is the main process. The isomerisation of the thiirane ring into an ethylenethiol form is observed only for bromine-substituted diphenylthiiranes. Divinylthiiranes also undergo intramolecular rearrangements. The high-temperature (up to 1000 °C) thermolysis of thiiranes results mostly in the cleavage of the C–S bond in the thiirane ring and its partial isomerisation into ethylenethiol rather than in elimination of sulfur. Unstable biradicals and thiyl radicals thereby formed undergo further decomposition into hydrogen sulfide, hydrocarbons and thiophene.¹²⁰

Four-membered sulfur-containing heterocycles are rather unstable. Thietane (trimethylene sulfide) decomposes on heating to 95 °C. Its thermal destruction in vacuum (250 °C, 10 Torr) leads to an oily polymer and small amounts of hydrogen sulfide, ethylene, ethane, propene and propane.^{117, 131} Thioformaldehyde is the product of the flash pyrolysis of thietane at 1000 °C.¹³³ Photolysis of thietane, 3-ethyl-2-propylthietane and 3-methylthietane in the gas phase, solution and glassy matrices was shown¹³⁴ to involve the cleavage of the C–S bonds and the formation of 1,4-biradicals. Derivatives of thiete (thiacyclobutene) undergo polymerisation even at room temperature. They are relatively stable only in solution.¹³⁵

Five-membered sulfur-containing heterocycles are more stable. Thiolane is stable below 450 °C. The extent of its decomposition at 500 °C is 10% and that at 550 °C is 60%; the products formed include thiophene, hydrogen sulfide and hydrocarbons. 1-Thiaindan decomposes at 450 °C into hydrogen sulfide and thiols.¹³⁶

Thermal decomposition of 2,5-dihydrothiophene at 600 °C leads to thiophene and hydrogen in the ratio of 1:1 along with hydrogen sulfide and polymeric products. Hydrogen is liberated in this reaction synchronously with other products.^{119, 137}

Benzo[b]thiophen-2(3*H*)-one is converted into benzothiophene on flash vacuum pyrolysis (700 °C, 0.05 Torr).¹³⁸

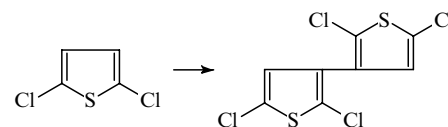


2,3-Dihydrothiophene-2,3-diones and their analogues eliminate CO on flash vacuum pyrolysis to form the corresponding thietones.¹³⁹

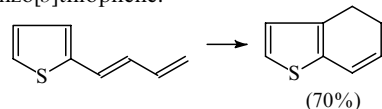
Thiophene is stable up to 800 °C, while at 850 °C it decomposes to give a mixture of isomeric bithienyls, benzothiophene, phenylthiophene (7%–8% overall yield) and gaseous products.¹⁴⁰ In a flow-recycling system, the yields of isomeric bithienyls, benzothiophene and phenylthiophene are 30%, 20% and 10%, respectively. Hydrogen sulfide accelerates the thermal transformation of thiophene into isomeric bithienyls, among which 2,3'- and 3,3'-isomers predominate (95% total yield).¹⁴¹

Hydrogen sulfide, thiophene and benzene are the main pyrolysis products of 2-methylthiophene at 825 °C. Aromatic compounds are formed in this reaction as the result of condensations of intermediate radicals and carbenes.¹⁴²

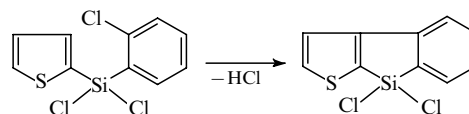
2,3-Dichlorothiophene undergoes the condensation into tetrachloro-3,3'-bithienyl at 560–570 °C.¹⁴³



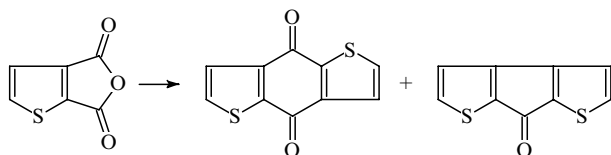
Vacuum pyrolysis of 1-(2-thienyl)buta-1,3-diene at 525–575 °C and 0.1–1.0 Torr leads to 4,5-dihydrobenzo[b]thiophene.¹⁴⁴



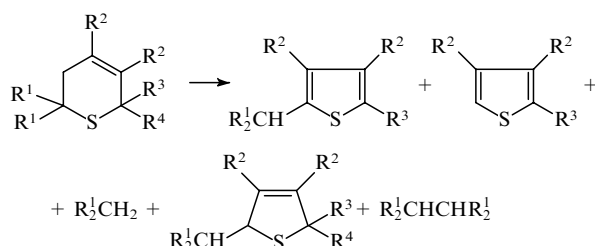
2-Chlorophenyl(2-thienyl)dichlorosilane undergoes heterocyclisation at 480–700 °C.¹⁴⁵



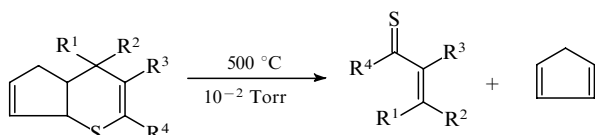
Vacuum thermolysis of thiophene-2,3-dicarboxylic anhydride at 500 °C (1–5 Torr) in a flow system leads to annelated thiophenes, which can be considered as analogues of anthraquinone and fluorenone.¹⁴⁶



Six-membered sulfur-containing heterocycles are less stable than thiophene and its derivatives. Under an argon atmosphere, dihydro-2*H*-thiopyrans undergo rearrangements into the corresponding thiophenes and dihydrothiophene on heating to 260 °C.¹⁴⁷

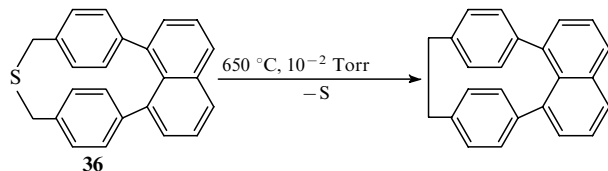


Fused dihydro-2*H*-thiopyrans undergo a retro-Diels–Alder reaction on flash vacuum pyrolysis.¹⁴⁸



Tetrasubstituted 4-thiapyrones rearrange into the corresponding 2-thiapyrones on heating to 200–250 °C.¹⁴⁹

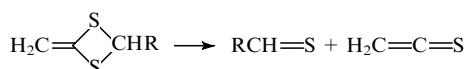
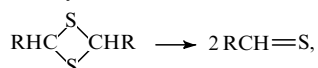
On flash vacuum pyrolysis, the polynuclear cyclic sulfide **36** eliminates the sulfur atom to form a cyclophane-like hydrocarbon.¹⁵⁰



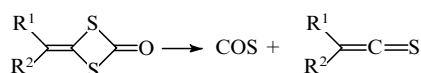
Benzothiophene and dibenzothiophene are fairly stable in the gas phase. Both the aromatic and thiophene rings are hydrogenated in the reaction of benzothiophene with atomic hydrogen at 150 °C. At 560 °C, only the thiophene ring is hydrogenated providing vinyl phenyl sulfide.^{151, 152} Octachloro-2,3-dihydrobenzothiophene is converted into hexachlorobenzothiophene at 200–250 °C.¹⁵³

Dibenzothiophene does not decompose up to 900 °C. Thianthrene decomposes partially at 550 °C to form dibenzothiophene and benzene. Due to the high stability of these heterocycles, not all sulfur from cyclic sulfides is lost on pyrolysis of coals.¹⁵⁴

The direction of the gas-phase thermolysis of dithiacycloalkanes and alkenes depends on the nature of the heterocycle. The vacuum thermolysis of 1,3-dithianes⁷⁷ and -dithietanes^{155, 156} at 300–750 °C leads to their cleavage into starting monomers, viz., thioaldehydes and thioketenes.

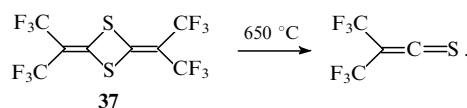


R = H, Ph.



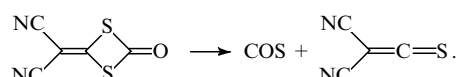
R¹ = CN; R² = CN, COMe, COOEt.

Bis(trifluoromethyl) thioketene is obtained on pyrolysis of its dimer **37** at 650 °C; it can be stored in a sealed tube for several months.¹⁵⁷ Hydrogen sulfide, tetrakis(trifluoromethyl)allene and perfluoroisobutylene are the other products of this reaction.



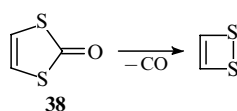
Thioketenes were characterised by photoelectron spectroscopy (PES) and isolated in the form of dimers or adducts of 1,3-dipolar cycloaddition reactions.

Dicyanothioketene is formed in the vacuum pyrolysis of 2-(4-oxo-1,3-dithietane-2-ylidene)malononitrile (470 °C, 0.05 Torr). However, this thioketene appeared to be extremely unstable and was characterised only by PES.¹⁵⁸

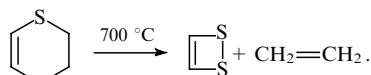


Dithiaspirocycloalkanes with five- and six-membered rings undergo pyrolysis at 600 °C to give cyclopentanethione or cyclohexanethione.¹⁵⁹ Ethylenedithioketal of quadricyclanone undergoes extensive fragmentation at 200 °C to form benzene and hydrogen sulfide.¹⁶⁰

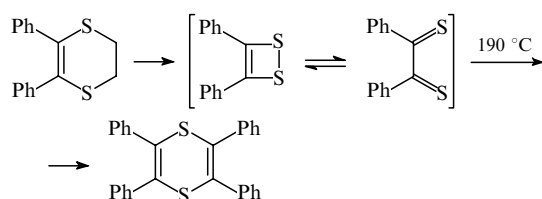
On flash pyrolysis, 1,3-dithiol-2-one (**38**) and its derivatives lose CO to give the corresponding dithietes.¹⁶¹



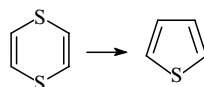
Dithiete and ethylene are formed in the flash vacuum pyrolysis of 2,3-dihydrodithiine at 700 °C.¹⁶¹



Flash pyrolysis of 1,2-diphenyl-5,6-dihydro-1,4-dithiine at 720 °C (0.1 Torr) involves the elimination of ethylene and leads to polymers which are converted into tetraphenyldithiine on heating in decalin.¹⁶² 1,2-Dithietes or α-dithiones are presumably the intermediate products in these reactions.

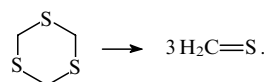


The main direction in the flash vacuum thermolysis of 1,4-dithiines at 700 °C involves the extrusion of sulfur and the formation of thiophene.¹⁶¹



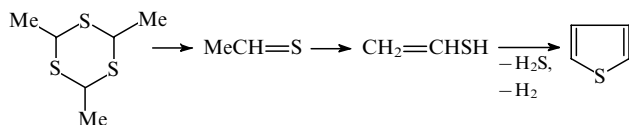
Substituted 1,4-dithiines eliminate sulfur even on heating to only 200 °C.^{163–165}

1,3,5-Trithiane and its derivatives decompose to the starting monomers on pyrolysis. Thus thioformaldehyde is formed from trithiane at 600 °C in vacuum.^{166, 167}

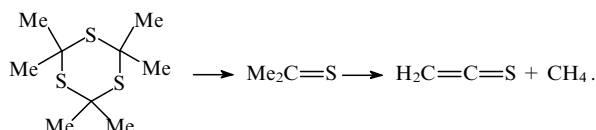


Pyrolysis of 2,4,6-trimethyl-1,3,5-trithiane at 600 °C in vacuum leads to monomeric thioacetaldehyde, which has a lifetime of

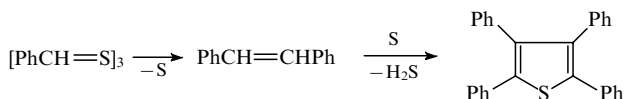
10 s;^{166, 167} at 450–600 °C and normal pressure; ethylenethiol and thiophene are formed. Thiophene is obtained as the result of the initial isomerisation of thioacetaldehyde and subsequent intermolecular condensation of ethylenethiol.¹⁶⁸



Vacuum pyrolysis of hexamethyltrithiane at 500 °C leads to thioacetone, while at 900 °C it yields thioketene, which results from the thermal decomposition of thioacetone.¹⁶⁹ Under ordinary conditions, monomeric thioacetone is stable for only a few minutes.



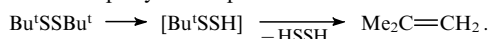
The fact that thiobenzaldehyde trimer and high-molecular-mass thiobenzaldehyde polymer decompose at 150 °C producing sulfur and stilbene from which tetraphenylthiophene is formed at 250 °C was established back in the past century.^{170, 171}



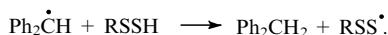
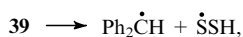
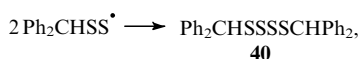
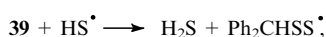
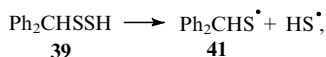
Heating of thioacetophenone trimer with rapid distillation of the thermolysis products yields monomeric thioacetophenone. The latter, as well as its trimer, is converted into 2,4-diphenylthiophene, stilbene and ethylbenzene on heating.¹⁷²

IV. Hydrodisulfides

Hydrodisulfides (RSSH) are unstable compounds and are often formed as intermediates in the thermolysis of organic disulfides. Thus the thermal decomposition of di(*tert*-butyl) disulfide apparently results in the initial formation of *tert*-butyl hydrodisulfide, which then rapidly decomposes into isobutene and H₂S.¹⁷³



Diphenylmethyl dihydrodisulfide (**39**) decomposes at 120 °C to form diphenylmethane, bis(diphenylmethyl) tetrasulfide (**40**) and hydrogen sulfide. The reaction involves the initial generation of thiyl radicals **41**, which further react with the starting hydrodisulfide according to a free-radical chain mechanism.¹⁷⁴



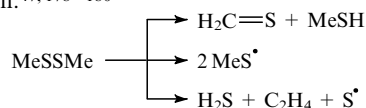
V. Disulfides

Organic disulfides are less stable than the corresponding sulfides and therefore readily undergo diverse transformations and react with organic compounds under the liquid- and gas-phase thermolysis conditions.

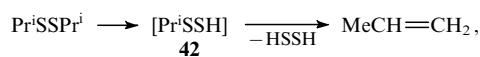
1. Dialkyl disulfides

Decomposition of dialkyl disulfides begins at temperatures approximately 200–250 °C lower than those required for the thermolysis of the corresponding sulfides.⁴⁵ Temperatures at which dialkyl disulfides decompose completely were determined by PES and decrease with an increase in the length and the branching of an alkyl chain in disulfides (from 1100 K for Me₂S₂ to 690 K for Bu₂S₂).⁵⁰

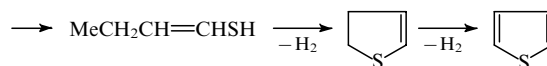
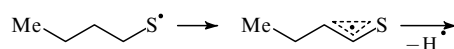
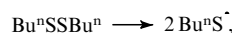
The corresponding thiols, alkyl sulfides, hydrogen sulfide, saturated and unsaturated hydrocarbons are the main products in the gas-phase pyrolysis of dialkyl disulfides at 500 °C. Also, a small amount of thiophene is formed.⁴⁹ At higher temperatures (580–610 °C), carbon disulfide is the major liquid product (23.5% yield) in the pyrolysis of dimethyl disulfide. From diethyl disulfide under the same conditions, carbon disulfide is formed in only 9.5% yield.¹⁷⁵ Flash vacuum pyrolysis of dimethyl disulfide at 300–700 °C leads to methanethiol and thioformaldehyde, while at 900 °C it mainly yields carbon disulfide.^{77, 176} The addition of methanethiol to the reaction does not affect its rate, whereas hydrogen sulfide substantially accelerates the pyrolysis of dimethyl disulfide.¹⁷⁷ Thioformaldehyde and methanethiol were detected and characterised by PES. Both molecular and radical mechanisms are assumed to be responsible for their formation.^{47, 178–180}



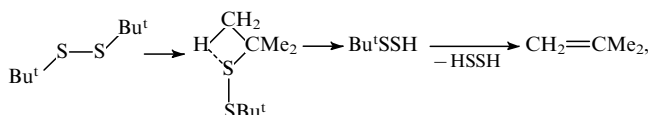
The reactions of thiyl radicals with the starting disulfide lead to its complete decomposition. Vacuum pyrolysis of diethyl disulfide occurs in a similar way.¹⁷⁸ Flash pyrolysis of diisopropyl disulfide presumably occurs through the stage of formation of isopropyl hydrodisulfide (**42**), since more stable propane-2-thiol was not found among the pyrolysis products.⁵⁰



A liquid product obtained upon gas-phase pyrolysis of di(*n*-butyl) disulfide at 500–550 °C represents pure thiophene (40%–60% yield). Gaseous hydrocarbons C₁–C₄ and hydrogen sulfide are the other products.¹⁸¹ The reaction mechanism involves the thermal generation of butylthiyl radicals and their intramolecular cyclisation into dihydrothiophene with its further dehydrogenation.^{137, 182}

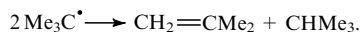
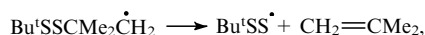
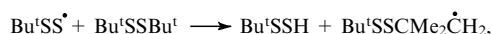


Gas-phase pyrolysis of di(*tert*-butyl) disulfide at 330–400 °C in both a flow and a static systems (60–212 Torr) leads to isobutene and *tert*-butyl hydrosulfide. The latter then decomposes into sulfur and hydrogen sulfide on the reactor walls.¹⁸³



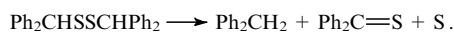
Carbon disulfide, hydrogen sulfide, acetylene and methane are formed at 1127 °C.⁴⁵ Since the C–S bond in di(*tert*-butyl) disulfide is weaker than the S–S bond, thiyl radicals are not formed. The initial cleavage of the C–S bond can only induce a short chain process



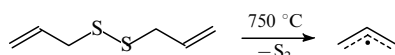


The formation of isobutane (5% and 13% yields in a flow and a static systems, respectively) confirms this scheme.⁴⁵

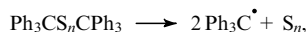
Thermal decomposition of bis(diphenylmethyl) disulfide at 150–200 °C leads to thiobenzophenone, diphenylmethane and sulfur. The reaction rate is increased with an increase in temperature.¹⁸⁴



Diallyl disulfide eliminates sulfur on flash pyrolysis. The allyl radical formed in this reaction was isolated in an argon matrix and characterised by UV, IR and EPR spectroscopy.¹⁸⁵

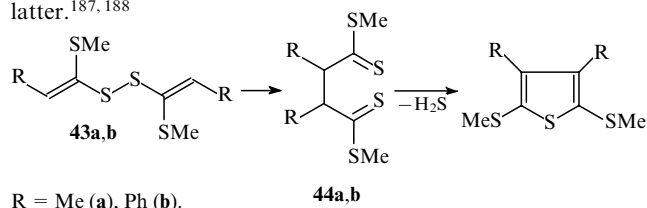


Bis(triphenylmethyl) polysulfides decompose on refluxing in benzene to form hexaphenylethane and sulfur. The thermal stability of $\text{Ph}_3\text{CS}_n\text{CPh}_3$ is decreased with the change in n as follows: $1 > 3 > 4 > 2$ (Ref. 186)

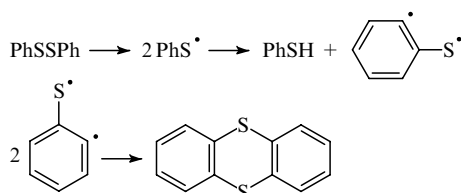


2. Unsaturated, aromatic and heteroaromatic disulfides

Bis(1-methylthiopropenyl) (**43a**) or bis(1-methylthio-2-phenylvinyl) disulfides (**43b**) cyclise into tetra-substituted thiophenes at 100–200 °C. The reactions involve a [3,3]-sigmatropic Cope rearrangement of compounds **43a,b** into the corresponding dithio esters **44a,b** and the elimination of hydrogen sulfide from the latter.^{187, 188}

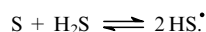
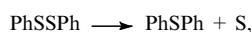
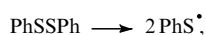


Benzenethiol and thianthrene are formed from diphenyl disulfide on heating to 260–300 °C in an inert atmosphere. This reaction follows a free-radical mechanism.¹⁸⁹



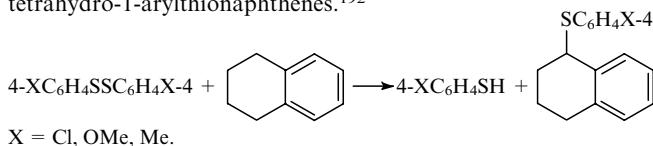
Analogous products are formed in the thermolysis of bis(4-methylphenyl) disulfide. The formation of phenethyl radicals in the vacuum pyrolysis of diphenyl and 2,2'-dinaphthyl disulfides (400–700 °C) was proved by EPR spectroscopy (in a liquid nitrogen matrix).¹⁹⁰

Thermolysis of diphenyl disulfide at 180–250 °C in an atmosphere of hydrogen sulfide leads to benzenethiol and diphenyl sulfide. The maximum yield of benzenethiol (52%) is achieved at 180 °C, while diphenyl sulfide is the major reaction product (82%) at 250 °C. Benzenethiol and diphenyl sulfide result from two parallel reactions.¹⁹¹

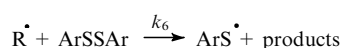
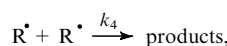
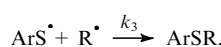
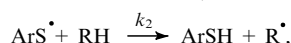
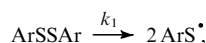


The liberation of sulfur in the thermolysis of diphenyl disulfide predominates at high temperatures and is apparently induced by hydrogen sulfide.

Thermolysis of diaryl disulfides in refluxing tetralin results in the formation of the corresponding arenethiols and 1,2,3,4-tetrahydro-1-arylthionaphthenes.¹⁹²



The following reaction mechanism has been suggested¹⁹²



RH is tetralin, $\text{R}^\bullet$ is a radical derived from tetralin.

The reaction is induced by arylthiyl radicals generated on the thermal dissociation of the S—S bond in diaryl disulfides. The arylthiyl radicals abstract the α -hydrogen from tetralin producing tetralinyl radicals, which react either with thiyl or other tetralinyl radicals. Based on the results of kinetic and UV studies, an assumption that arylthiyl radicals are π -radicals has been put forward.¹⁹²

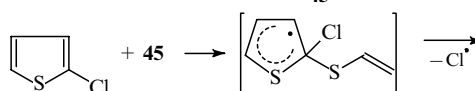
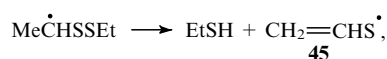
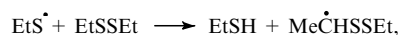
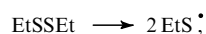
Diphenyl disulfides with substituents in the *para*-positions of the benzene rings decompose more rapidly. The order in the change in the reaction rates depending on the nature of substituents ($\text{MeO} > \text{Cl} \simeq \text{Me} > \text{H}$) correlates with the stability of the respective thiyl radicals. The latter is increased with the strengthening of the resonance interaction between the substituent and the benzene ring.

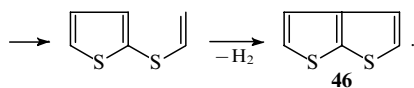
Di(2-thienyl) disulfide eliminates sulfur to form di(2-thienyl) sulfide on heating to 130–180 °C in an atmosphere of hydrogen sulfide.¹⁹³

3. Thermal reactions involving disulfides

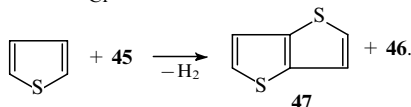
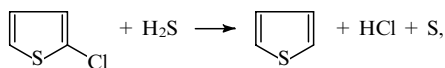
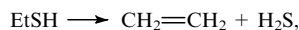
Thiyl radicals generated on thermal decomposition of dialkyl disulfides can substitute the halogen atom at the sp^2 -hybridised carbon atom and add to the triple bond of acetylene and its derivatives. These reactions predominantly yield heterocyclic compounds of the thiophene series.

The gas-phase reaction of 2-chlorothiophene with diethyl polysulfides at 560 °C leads to a 4:1 mixture of thieno[2,3-*b*]thiophene (**46**) and thieno[3,2-*b*]thiophene (**47**) (in up to 33% overall yield). Thieno[2,3-*b*]thiophene is formed as the result of the addition of vinylthiyl radicals **45** generated from diethyl polysulfides to 2-chlorothiophene and subsequent heterocyclisation.⁵⁵



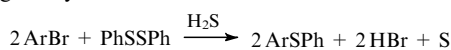


Both isomeric thienothiophenes are formed in parallel addition reactions of vinylthiyl radicals to thiophene. The latter is obtained on reduction of 2-chlorothiophene with hydrogen sulfide



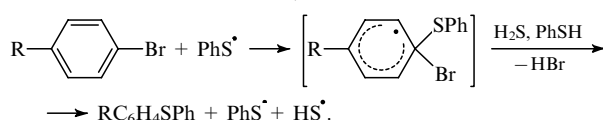
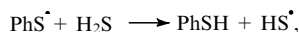
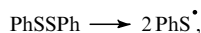
Chlorobenzene reacts with dialkyl disulfides in the gas phase in a similar way.¹⁹⁴

Aryl bromides effectively react with a diphenyl disulfide–hydrogen sulfide system at 125–240 °C to form aryl phenyl sulfides (49%–84% yields).¹⁹⁵ The reactions occur at a lower temperature if a π -donating substituent is present in the benzene ring of aryl bromides.

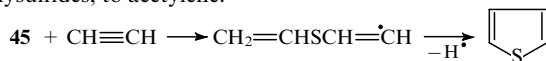


Ar = Ph, 2-HOC₆H₄, 4-HOC₆H₄, 4-EtC₆H₄, 4-CNC₆H₄, 1-naphthyl, 2-hydroxy-1-naphthyl.

Phenyl radicals generated from diphenyl disulfide substitute the bromine atom in aryl bromides, thus inducing the reactions. These radicals are generated again in the reaction chain propagation stage, playing also a role as hydrogen atom acceptors from hydrogen sulfide.¹⁹⁵



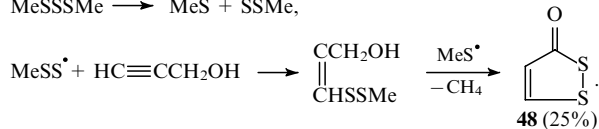
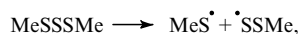
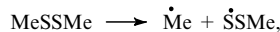
Dialkyl polysulfides react with acetylene in the gas phase at 470–520 °C to form thiophene (up to 60% yield) and isomeric thienothiophenes. Thiophene arises as the addition product of vinylthiyl radicals **45**, generated on the thermolysis of dialkyl polysulfides, to acetylene.¹⁹⁶



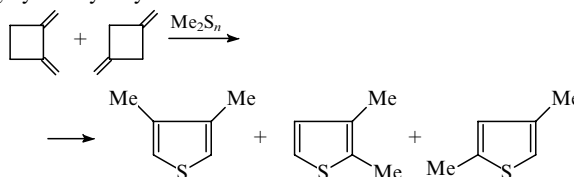
Isomeric thienothiophenes **46** and **47** are formed due to the addition of vinylthiyl radicals **45** to thiophene. The so-called ‘disulfide oil’ representing a mixture of dimethyl, diethyl and ethyl methyl disulfides can be used instead of diethyl disulfide in the reaction with acetylene. On pyrolysis, all these disulfides generate vinylthiyl radicals **45**, which then are trapped by acetylene.¹⁷⁵ However, the yield of thiophene in this case is lower than that obtained from pure diethyl disulfide.¹⁹⁷ If a mixture of diethyl disulfide and diethyl selenide is used in the reaction with acetylene, the yield of thiophene is increased up to 92%.¹⁹⁸

The reaction of 2-chlorothiophene with a diethyl disulfide–acetylene system at 650–700 °C leads to thiophene and thieno[2,3-*b*]thiophene (**46**).¹⁹⁹ Thiophene results from the reaction of acetylene with the vinylthiyl radicals **45**. Thieno[2,3-*b*]thiophene (**46**) is formed due to the reaction of acetylene with 2-thienylthiyl radicals **16** generated *in situ* from 2-chlorothiophene and hydrogen sulfide (the thermolysis product of diethyl disulfide). Acetylene is a more efficient scavenger of thiyl radicals than 2-chlorothiophene; its addition suppresses the competing reaction leading to di(2-thienyl) sulfide.¹⁹⁹

The gas-phase reaction of dimethyl di- or trisulfide with propargyl alcohol at 500 °C leads to 1,2-dithiol-3-one (**48**).²⁰⁰ In this reaction, propargyl alcohol acts as a scavenger of MeSS[•] radicals

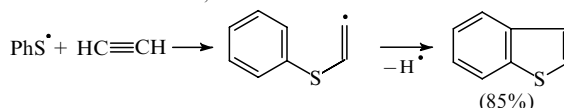
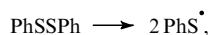


Dimethylthiophenes (a mixture of 3,4-, 2,3- and 2,4-isomers) are the main products in the gas-phase reaction of dimethyl di- or trisulfide with a mixture of 1,2- and 1,3-dimethylenecyclobutanes at 450–500 °C.²⁰¹ The reaction involves cyclobutane ring-opening by methylthiyl radicals.



$n = 2, 3$.

Benzo[*b*]thiophene is selectively formed in the gas-phase reaction of diphenyl disulfide with acetylene at 500 °C.²¹



In the gas phase, acetylene reacts with 1,1-dinaphthyl disulfide in the same way as it does with naphthalene-1-thiol (see Section II.2).³⁵

VI. Conclusion

Thus, as can be seen from the data presented here, the thermal reactions of organic compounds of divalent sulfur produce both thiyl radicals and such highly reactive intermediates as thioformaldehyde and its homologues, ethylenethiol, thioketene, etc.

Further transformations of these intermediates and their reactions with thiyl radicals and organic additives result in a great variety of the products obtained on thermolysis and pyrolysis of sulfur-containing organic compounds. Many of these processes are highly selective and can be used for the synthesis of compounds inaccessible by other methods.

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Thermodynamic properties of C₆₀ and C₇₀ fullerenes

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Abstract. The most reliable values of the basic thermodynamic parameters of the C₆₀ and C₇₀ fullerenes are recommended based on the analysis of the published data and original calculations, viz., enthalpies of formation in the solid and gaseous states, saturated vapour pressures, enthalpies of sublimation, enthalpies of phase transitions, heat capacities, entropies in the condensed state and heat capacities and entropies in the ideal gas state. The factors influencing the results of thermodynamic studies of fullerenes are discussed. Various aspects of crystal structure determination, PVT-relationships and frequencies of normal modes of the C₆₀ and C₇₀ fullerenes are considered in order to interpret and correlate the thermodynamic data and extend them to a wide temperature range. The bibliography includes 135 references.

I. Introduction

The need for the knowledge of thermodynamic properties of fullerenes arises not only from the interest in this unusual class of compounds or the quest for efficient ways of their preparation and practical use. The fullerenes have now become the 'proving ground' for testing virtually all the modern methods of predicting the structure and properties of solids, fluids and ensembles of particles. Therefore, the well-grounded and reliable values of the basic thermodynamic parameters of these compounds are of great importance. Although the extensive literature on fullerenes is available (including reviews^{1–5}), their thermodynamic properties are known less reliably than those of many other 'ordinary' compounds. The publication of a specialised review⁶ devoted to the studies of thermodynamic properties of fullerenes was followed by the appearance of many new communications. However, their results were often contradictory. The main reason for the contradictions seems to lie in the specific properties of fullerenes, which are more sensitive to the sample prehistory and conditions of the experiment than the properties of ordinary organic substances. Understanding of this fact came gradually in the course of thermodynamic and other studies, so that the lack of information at the time of publication of an article often did not enable the

authors to assess the influence of various factors on the final result of their measurements. Therefore, any report on thermodynamic properties of fullerenes should be considered in the light of the overall information available on these compounds with the details of the experiment taken into account.

Based on such an analysis (the experimental data published between 1987 and 1998 have been surveyed), the present review recommends values for the most important thermodynamic parameters of the C₆₀ and C₇₀ fullerenes. The following criteria were used in selecting the experimental data and establishing the recommended values. The characterisation of samples and experimental procedures should be exhaustive in order to rule out the influence of known factors affecting the results of measurements. Preference was given to the results available for the sublimates whose purity and stability were confirmed by independent studies. The precision of the techniques used and reproducibility of the results were taken into account. Thus the heat capacity values measured by adiabatic calorimetry (AdC) were considered to be the most reliable. An agreement between the results obtained by various authors as well as between the thermodynamic parameters of each of the fullerenes were also taken into consideration.

II. Behaviour of fullerenes in thermodynamic studies

The effect of impurities and chemical instability of fullerenes are the factors that hamper the determination of their thermodynamic properties most seriously. Conventional purification procedures and methods of purity control applied to organic compounds appeared to be inefficient for fullerenes which show a tendency towards co-crystallisation with the solvent molecules. Even small amounts of impurities significantly affect various properties of fullerenes. Thus, the phase transition temperature⁷ (T_{tr}) of C₆₀ shifts from 260.7 K to 243 K or to 245 K in the presence of benzene⁸ or toluene admixtures. Also an additional heat capacity anomaly appears at 232 or 239 K, respectively. Two additional heat capacity anomalies,⁹ at 185 and 425 K appear in the C₆₀ sample crystallised from carbon disulfide due seemingly to the presence of a CS₂ impurity. The anomaly observed at 185 K disappears after annealing the sample at 425–500 K. The C₆₀ crystals grown from a solution of fullerene in carbon disulfide are monoclinic, the temperature of the 'ordinary' phase transition being shifted in such crystals to 242 K.¹⁰ The rhombohedral C₆₀ crystals grown from a toluene–hexane solution (the purity is 99.9% from mass spectrometric measurements) undergo a phase

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transition associated with a diffuse anomaly of the heat capacity at 239 K.¹¹ It was found that an adduct of the C₇₀ fullerene with toluene (C₇₀·C₇H₈) exhibits heat capacity anomalies at 195 and 430 K (the latter is due to an irreversible decomposition of the adduct).¹² After the decomposition of the adduct, a heat capacity anomaly¹² at 304 K and two phase transitions¹³ at 277.4 and 340.0 K were observed in the sample. It was also found out that several heat capacity peaks observed upon phase transition in C₆₀ are due to the C₇₀ impurity present in the sample.¹⁴

It was found that fullerenes absorb (or adsorb) large amounts of oxygen and, probably, water.¹⁵ Pellet-like samples were kept in a moist oxygen atmosphere under pressure of 30 bar. It was measured that C₆₀ absorbs 30–60 g mol^{−1} in 0.5 h and C₇₀, more than 150 g mol^{−1} in ~24 h. Although these estimates¹⁵ are seemingly overstated (the specific surface of the C₆₀ samples measured with liquid nitrogen¹⁶ was ~3 m² g^{−1}), the uncontrolled adsorption could affect the results of combustion experiments. Two maxima on the temperature curve of desorption of oxygen and other substances plotted for a C₆₀ sample indicate¹⁷ that impurities are absorbed by both the surface and the bulk of a substance. The location of impurities in polycrystalline fullerene C₆₀ has been studied in detail;¹⁶ it was found that the solvent molecules were mainly adsorbed on the surface of microcrystals, whereas upon thermal treatment, they could be fixed in cavities of the baked crystals. This may be a reason why it is difficult to purify fullerenes by heating *in vacuo*.

The thermodynamic properties of fullerenes were reported to depend on the size of crystals in a sample.^{18–21} A finely crystalline C₆₀ sample (**1**) of brown colour which contained 0.004 mol of C₇₀ (from HPLC measurements) exhibited a fall in the phase transition temperature ($T_{tr} = 258.6$ K), a decrease in the enthalpy of combustion ($\Delta_c U^\circ = -35\,896$ J g^{−1}) and incomplete yield of CO₂ in the combustion products (approximately 99.8%) as compared to similar characteristics ($T_{tr} = 260.9$ K; $\Delta_c U^\circ = -36\,030$ J g^{−1}; the yield of CO₂ upon combustion is 100.00 ± 0.04%) exhibited by a chromatographically pure coarsely crystalline C₆₀ sample (**2**) of black colour.²¹ Both samples were dried under the same conditions: for several hours at 440–520 K and a pressure of 0.001 Pa. Kolesov *et al.*²¹ suggest however that the changes in the properties of the sample **1** could be caused by impurities either occluded upon its fast crystallisation or adsorbed by its developed surface.

It was found^{19,20} that the C₆₀ crystals become progressively less capable of solid-state transitions as they are ground. Skokan *et al.*¹⁶ examined this phenomenon in detail to conclude that this results from the defects accumulated in the crystals, the effect of solvent impurity not being involved.

At fairly high temperatures (700 K and above) at which most of the reported effusion measurements have been made, partial decomposition of samples can occur. Thus, a nonvolatile residue (8%) was detected in C₆₀ after it had been sublimed at 1273 K in a nitrogen atmosphere and dried *in vacuo* at 700 K.²² A sample of C₆₀ purified by sublimation at 673 K (the sample purity was 99% from mass spectrometric measurements²³) yielded 5% of a nonvolatile residue after it had been sublimed at 973–1073 K in a nitrogen or an argon atmosphere. After sublimation of the 99.98% pure C₆₀ fullerene, 0.1%–0.3% of the substance still remained nonvolatile, the evaporation of the first half of the sample being followed by a not fully understood fall of the saturated vapour pressure.²⁴ It is suggested that partial transformation of fullerenes into nonvolatile amorphous carbon at 700–740 K may result from contamination of the initial sample with remains of organic solvents.²⁵ Fullerene C₇₀ (98.5% pure, the main impurity being C₆₀) contained 6%–8% of nonvolatile deposit (amorphous carbon) after mass loss of 1% had been detected at 450 K and a cycle of effusive measurements had been performed.²⁶ A sublimed sample was evaporated nearly completely in a repeat run, although some pressure fall was observed in the effusive measurements in carbon cells at 800–900 K and a small amount of nonvolatile deposit was still detected. Destruc-

tion of the C₆₀ and C₇₀ fullerene molecules in the vapour phase²⁷ begins at 2650 and 2440 K, respectively, and in the condensed state,^{28,29} above 1000–1073 K, the temperature limits depending on the nature and content of impurities.²⁵

Therefore, the following strategies appear to be efficient in the preparation of pure specimens suitable for thermodynamic studies: growth of large-sized crystals^{16,21} and sublimation of fullerenes *in vacuo*.^{24,26,30,31} If, prior to sublimation, a sample is dried at a gradually increasing temperature, the major portion of the solvent is probably removed before the degradation (amorphisation) of the basic substance begins.

Experience gained by various researchers suggests^{15,17} that the protection from traces of oxygen is particularly necessary in the sublimation. Fullerenes are known to be vigorously oxidised by oxygen at elevated (> 500 K) temperatures.^{23,32–34} However, under exposure to either high-energy photons or visible light (0.5–5.0 eV), the photoinduced oxidation of the fullerenes by atmospheric oxygen becomes possible at room and even low (20 K) temperatures.³⁵ This imposes additional requirements for the preparatory conditions and purification of fullerenes intended for thermodynamic studies.

Methods of purity control of the samples used for thermodynamic measurements are of principal importance. HPLC is a traditional method which allows determination of the degree of separation of fullerenes with different compositions and the C₆₀O content.¹⁵ It is significant to establish to what extent the organic solvents used for the sample preparation (benzene, toluene, xylene, carbon disulfide, diethyl ether, *etc.*) have been removed. The presence of benzene impurity is determined using ¹H NMR,³⁶ although the sensitivity of the method may be insufficiently high.³⁷ The hydrogen content in a C₆₀ sample is measured by activation analysis.³⁸ The C₆₀ sample was heated in a sealed tube in a nitrogen atmosphere (673 K, 10 min) and the vapour phase was then analysed by GLC.³⁹ Unfortunately, total removal of impurities as well as their constant chemical composition are questionable under such conditions. Volatile substances released upon gradual heating of a C₆₀ sample were analysed by mass spectrometry,¹⁷ but no quantitative estimates of the impurity content were made. The phase transition temperatures and a proportion of nonvolatile deposit found after the sublimation may serve as indirect criteria of the sample purity.

The lack of details in some papers describing the prehistory of samples and methods of their study does not enable one to evaluate the effect of the above-listed factors on the results of measurements of thermodynamic properties.

III. Enthalpies of formation of C₆₀ and C₇₀

The measured enthalpies of combustion and formation of C₆₀ are listed in Table 1. The scatter in the standard combustion energies amounts to ~0.6% (from −35 914 to −36 124 J g^{−1}) which is

Table 1. The enthalpies of combustion and formation of C₆₀.

$-\Delta_c U^\circ$ / J g ^{−1}	$-\Delta_c H^\circ$ / kJ mol ^{−1}	$\Delta_f H^\circ$ / kJ mol ^{−1}	Ref.
35 914.0 ± (18.0)	25 881.8 ± (13.0)	2273.0 ± (13.0)	36
35 923.6 ± (16.8)	25 888.7 ± (12.1)	2278.1 ± (14.4)	38
35 929.5 ± 19.4	25 893.0 ± 14.0	2282 ± 16	43
35 992 ± 61	25 938 ± 44	2327 ± 44	15
36 004.6 ± (11.8)	25 947.1 ± (8.5)	2336.5 ± (8.5)	42
36 030 ± 16	25 965 ± 12	2355 ± 15	21
36 036.7 ± 16.7	25 970 ± 12	2360 ± 16	39
36 123.7 ± (19.4)	26 032.9 ± (14.0)	2422.3 ± (14.0)	37
36 017 ± 17	25 956 ± 12	2346 ± 12	

Note. Here and in Table 2, the recommended values are printed in bold face. We estimated the uncertainties within the reliability interval of 95%. The errors given in parentheses are taken from the reference cited; they are most commonly twice the standard deviation.

Table 2. The enthalpies of combustion and formation of C₇₀.

$-\Delta_c U^\circ / \text{J g}^{-1}$	$-\Delta_c H^\circ / \text{kJ mol}^{-1}$	$\Delta_f H^\circ / \text{kJ mol}^{-1}$	Ref.
35 587±(25)	29 921±(36)	2375±(36)	36
35 629.4±(10.6)	29 956.1±(8.9)	2410.4±(8.9)	42
35 664±44 ^a	29 985±37 ^a	2439±37 ^a	44
35 733±42 ^b	30 042.8±35.3 ^b	2497±35 ^b	
35 802±26	30 101±22	2555±22	15
35 828.4±15.8	30 123.5±13.4	2577.8±16.2	45
35 802±26	30 101±22	2555±22	

^a From the mass of a substance; ^b from the mass of CO₂.

more than an order of magnitude higher than the experimental error of measurement by combustion calorimetry of organic substances without heteroatoms. The reasons for such a scatter may be the factors that counteract each other, *e.g.*, organic solvent impurities like toluene which are characterised by the heats of combustion of large absolute values (-42382 J g^{-1}) and adsorbed oxygen and water which increase the apparent weight of a sample. The problems of precise determination of the enthalpies of combustion of fullerenes are discussed in a review,⁴⁰ and the enthalpies of formation of carbon clusters in relation to their structures and sizes are analysed in a review.⁴¹ The scatter of the reported enthalpies of combustion $\Delta_c H^\circ$ lies within 0.12%,^{15,21,39,42} The results of earlier publications lie outside this interval. Five experiments performed on presumably one of the best C₆₀ samples (purified by sublimation)¹⁵ gave, for unclear reasons, a wide dispersion of the results. Kolesov *et al.*²¹ examined a specially prepared coarsely crystalline sample; an analysis of the combustion products gave the CO₂ yield of $100.00 \pm 0.04\%$. A similar result was obtained³⁹ (see Table 1) using large samples (of approximately 0.5 g) and an original GLC-analysis of organic solvent contaminations in fullerene (0.013 mass % of diethyl ether and 0.007 mass % of *o*-xylene). Later, An *et al.*⁴² gave the enthalpy of C₆₀ combustion which was slightly different from their previous result.³⁹ Therefore, the value $\Delta_f H^\circ(\text{cr}) = 2346 \pm 12 \text{ kJ mol}^{-1}$ which is an average of the published data^{21,42} is recommended for the enthalpy of formation of C₆₀ in the crystalline state.

The enthalpy of formation in the gaseous state is $\Delta_f H^\circ(\text{g}) = 2530 \pm 13 \text{ kJ mol}^{-1}$, the enthalpy of sublimation of C₆₀ ($\Delta_{\text{sub}} H^\circ = 183.7 \pm 5.1 \text{ kJ mol}^{-1}$) being taken into account.

The measured combustion energy values $\Delta_c U$ for the C₇₀ fullerene (Table 2) are scattered even wider, over more than 0.7% (from $-35 587$ to $-35 828 \text{ J g}^{-1}$). The reasons for the scatter are evidently similar to those for C₆₀. The uncertainty of the crystal composition of C₇₀ at 298.15 K which is discussed

below cannot have a notable effect on the error in determination of the enthalpy of formation, because the energy difference between different crystal modifications of C₇₀ is two orders of magnitude smaller. It is likely that the best sample of this fullerene purified by sublimation was studied by Beckhaus *et al.*,¹⁵ therefore their results are recommended as most reliable. Only in one publication⁴⁴ was the amount of CO₂ in the combustion products measured to find a yield of $99.81 \pm 0.02\%$. Assuming that the material balance on carbon⁴⁴ was upset due to the presence of inert impurities (adsorbed gases or water) in the C₇₀ finely crystalline sample and relating the heat of combustion to the appropriate amount of CO₂, one obtains the value $\Delta_c U^\circ = -35 732.5 \pm 42 \text{ J g}^{-1}$, which is close to that given by Beckhaus *et al.*¹⁵ The data by Diogo *et al.*⁴⁵ are also close to the latter value¹⁵, but one cannot say, judging from the results of HPLC analysis of C₇₀ fullerene,⁴⁵ whether toluene was completely removed from the sample. We cannot offer an explanation of a low absolute value of the enthalpy of C₇₀ combustion reported by An *et al.*⁴²

Thus, the recommended value for the enthalpy of formation¹⁵ of C₇₀ is $\Delta_f H^\circ(\text{cr}) = 2555 \pm 22 \text{ kJ mol}^{-1}$. With the enthalpy of sublimation of C₇₀ $\Delta_{\text{sub}} H_{298.15}^\circ = 200.3 \pm 6.1 \text{ kJ mol}^{-1}$ taken into account, the enthalpy of formation in the gaseous state at 298.15 K is $\Delta_f H^\circ(\text{g}) = 2755 \pm 23 \text{ kJ mol}^{-1}$.

IV. Heat capacities in the condensed state and thermodynamics of phase transitions in C₆₀ and C₇₀

It is now commonly accepted that the C₆₀ fullerene crystallises at $T = 298.15 \text{ K}$ and pressure $P = 1 \text{ atm}$ in a face-centred cubic lattice with $a = 14.152 \text{ \AA}$ and $d = 1.69 \text{ g cm}^{-3}$ (see Ref. 17). Molecular rotation in such a crystal results in an orientational disorder. Upon cooling below 260 K, a solid-state transition occurs. In the low-temperature modification,^{46,47} the C₆₀ molecules have four different orientations in space making a simple cubic lattice. Some rotational degrees of freedom are retained in this case. The remaining rotational degrees of freedom freeze upon vitrification of the crystal⁴⁸ at around 90 K. From calorimetric measurements, the vitrification temperatures are $T_g = 86.8$ (see Ref. 49) and 86.0 K (see Ref. 7). The residual entropy of C₆₀ at 0 K was estimated to be 4.7 ± 0.5 (see Ref. 50) and $4.9 \text{ J K}^{-1} \text{ mol}^{-1}$ (see Ref. 7). Although the estimation procedures are not indisputable, we see little reasons for revising the results. As reported by Willart *et al.*,⁵¹ no other transitions occur in an impurity-free C₆₀ sample at atmospheric pressure.

Table 3 lists the measured enthalpies of phase transition $\Delta_{\text{tr}} H$ in C₆₀ around 260 K. Probable reasons for the scatter in T_{tr} and

Table 3. Thermodynamic characteristics of a solid-state transition in C₆₀.

T_{tr} / K	$\Delta_{\text{tr}} H / \text{kJ mol}^{-1}$	Sample	Method	Note	Ref.
249	4.8	purity 99.5%	DSC		52
255	6.7	dried <i>in vacuo</i> at 700 K	AdC	sample of small weight, 8% of a deposit detected after sublimation in nitrogen at 700 K	22
256	7.0	dried <i>in vacuo</i> at 475 K, purity 99.5% ^a	DSC		53
257.6	7.54	—	AdC		49
258	6.2	—	DSC	three peaks at 253, 258 (90%) and 260 K	54
259	3.2±0.2	—	DSC	peaks at 240 K (due to impurities) and 259 K; difficulty in baseline location	27
260	7	dried at 440 K (13 Pa, 5 days)	DSC		47
260.7	7.46±0.15	dried <i>in vacuo</i> at 400 K, purity 99.98% ^b	AdC		7
261.4	9.0±0.5	sublimed, single crystal	DSC	sample of small weight, the heat effect under the peak is 6.8 kJ mol^{-1} (see ^c)	19

Note. DSC is differential scanning calorimetry, AdC is adiabatic calorimetry. ^a From mass spectra and Raman spectra; ^b from HPLC measurements; ^c the remaining part of the heat effect (2.2 kJ mol^{-1}) was found by integrating the difference between the heat capacity of a sample and the baseline in the temperature interval 150–290 K.

Table 4. Details of heat capacity measurements of C_{60} in the condensed state.

Sample	Method	Temperature range /K	Ref.
Not completely solvent-free	AdC	10–300	8
Extracted with benzene, chromatography, dried at 700 K, 8% of a deposit detected after sublimation	AdC	4.2–300	22
Extracted with a benzene–hexane mixture, chromatography, washed with ether, dried at 475 K, 99.5% pure ^a	DSC	120–560 ^b	53
Extracted with toluene, washed with ether, chromatography, dried at 450 K for 50 h, purity 99.99 mol.% ^c	DSC	300–800	37
–	thermal relaxation	1.4–20	56
–	AdC	13–300	49
Extracted with a benzene–hexane mixture, chromatography, dried at 523 K for 24 h, single crystal	MC	120–300	11
Extracted with toluene, chromatography, dried at 400 K, 99.98 % pure ^d	AdC	5–339	7

Note. MC is modulation calorimetry. ^a From mass spectra and Raman spectra; ^b no phase transitions occur upon further heating to 950 K; ^c from HPLC measurements; ^d from HPLC and X-ray diffraction.

$\Delta_{tr}H$ values were discussed in Section II. In addition, the transition is not isothermal (2N-type according to the classification of Westrum and McCullough⁵⁵), which makes difficult both the interpretation of the calorimetric data and the choice of the heat capacity baseline in the calculation of the enthalpy of phase transition. This seems to account for the large value of $\Delta_{tr}H$ reported by Dworkin *et al.*¹⁹ The values^{7,49} of $\Delta_{tr}H$ measured by an adiabatic calorimetry are in good agreement with each other. The values measured in 1993 using differential scanning calorimetry (DSC) are fairly close to them.^{19,47,54} For the calculation of the entropy of the crystalline C_{60} , one should know the value of $\Delta_{tr}H$ together with the heat capacity values, which rules out the use of $\Delta_{tr}H$ averaged over several published data. Therefore, we recommend the values⁷ $T_{tr} = 260.7$ K and $\Delta_{tr}H = 7.46 \pm 0.15$ kJ mol^{−1} which are consistent with the heat capacity values recommended in the same publication.⁷

The heat capacities of C_{60} samples of different qualities measured by various methods are listed in Table 4. All the published results except for the data given in Refs 7, 37, 53 were presented only in a graphical form to show a fairly good agreement with each other (except for the data³⁷). Thus, the recommended values of thermodynamic parameters for the solid C_{60} in the interval 0–1000 K (Table 5) were listed based on the heat capacities measured by AdC⁷ in the range 5–340 K and by DSC⁵³ in the range 340–560 K. Because the Debye characteristic temperature of fullerenes is low, it is important to know their heat capacity below 5 K. Allowance is made in Table 5 for the heat capacities of C_{60} in the range 0–10 K which were measured by a thermal relaxation method (the graphical data⁵⁶). We extended the heat capacity values to the interval 560–1000 K by a procedure described by Jin *et al.*⁵³ The heat capacity C_V of a crystal was represented by a sum of contributions of the lattice (C_{lat}) and intramolecular (C_{int}) vibrations

$$C_V = C_{lat} + C_{int}.$$

The contribution of the intramolecular vibrations was calculated by methods of statistical thermodynamics using the set of normal modes chosen as described in Section VI. The contribution of the lattice translational modes at $T > 298.15$ K was taken to be $3R$, whereas that of the librational modes (or molecular rotation in a crystal) was calculated for the hindered rotation of the C_{60} molecules using a harmonic potential. The effective value of the potential barrier to molecular rotation (5 kJ mol^{−1}) was chosen to provide the best fit of the calculated heat capacities with their measured values in the range 300–560 K. A relatively low value of the potential barrier is qualitatively consistent with both

the spherical shape of the C_{60} molecule and the absence of heat capacity jump upon the solid-phase transition.⁵⁷

Table 5. Recommended values of the thermodynamic parameters [C_P , S and $-(G-H_0)/T$ in J K^{−1} mol^{−1}; $H-H_0$ in kJ mol^{−1}] of the crystalline C_{60} .

T /K	C_P	S	$-(G-H_0)/T$	$H-H_0$
Vitreous crystal II				
0	0	4.9	4.9	0
5	2.37	5.7	5.1	0.0030
10	13.78	10.4	6.4	0.0399
20	33.41	26.9	12.4	0.2887
50	49.72	65.5	33.8	1.586
86.0	76.62	97.4	53.8	3.744
Crystal II				
86.0	76.62	97.4	53.8	3.744
100	96.60	110.6	60.8	4.974
150	185.5	165.4	86.2	11.88
200	303.3	234.5	114.3	24.04
250	423.1	315.1	146.3	42.20
260.7	446.8	333.3	153.6	46.85
Crystal I				
260.7	446.8	361.9	153.6	54.31
298.15	525.6	427.1	183.8	72.52
300	529.6	430.3	185.3	73.50
350	633.6	520.1	226.7	102.7
400	720.5	610.4	269.0	136.6
450	801.9	700.0	311.9	174.6
500	877.7	788.5	355.2	216.6
550	947.8	875.5	398.5	262.3
600	1009	960.6	441.8	311.3
650	1062	1044	485.0	363.1
700	1107	1124	527.7	417.3
750	1147	1202	570.1	473.7
800	1180	1277	611.9	531.9
850	1210	1349	653.2	591.6
860	1215	1363	661.4	603.8
900	1236	1419	693.8	652.8
950	1259	1487	733.8	715.2
1000	1281	1552	773.0	778.7

Table 6. The α and β parameters of the C₆₀ fullerene.

T/K	$10^5 \alpha / K^{-1}$	$10^{10} \beta / Pa^{-1}$	Method	Ref.
298	—	0.7	X-ray structural analysis	58
323–523	27 ^a	1.4–2.5 ^a	dilatometry of powder	59
298.15	—	1.47	dilatometry	60
260–300	4	—	capacitance dilatometry	48
298	6.2±0.2	—	X-ray structural analysis	61
298	3.5	0.70	calculation	62
300–900	4.57±0.04	—	X-ray structural analysis	63
298	—	1.5	the same	64

^a A 3 : 1 mixture of C₆₀ and C₇₀.

C_P was calculated from C_V by the relationship

$$C_P - C_V = \frac{\alpha^2}{\beta} V_m T,$$

where α is the volume expansion coefficient, β is the isothermal compressibility coefficient, V_m is the molar volume. The following values were accepted for α and β at 300 K: $\alpha = 4.6 \times 10^{-5} K^{-1}$, $\beta = 1.55 \times 10^{-10} Pa^{-1}$ (Table 6). At this temperature, the difference $C_P - C_V$ was as low as $1.8 J K^{-1} mol^{-1}$, which appeared to be much less than the value estimated by Jin *et al.*⁵³. The difference $C_P - C_V$ was extended to $T = 1000 K$ using the procedure described by the same authors

$$C_P - C_V = k C_V T, \quad (1)$$

the value of k ($1.16 \times 10^{-5} K^{-1}$) was calculated from the data at 300 K.

The calculated heat capacities of the C₆₀ crystal (Fig. 1) are in good agreement with those measured by DSC⁵³ in the interval 500–550 K, whereas at 300 K, they are $11 J K^{-1} mol^{-1}$ (or $\sim 2\%$) less than the values measured by AdC.⁷ We estimate the error of the entropy determination of C₆₀ to be ± 2 and $\pm 13 J K^{-1} mol^{-1}$ at 298.15 and 860 K, respectively.

The Debye characteristic temperature of C₆₀ estimated from the heat capacity measurements in the interval 0–5 K amounts to $\sim 46 K$, which is close to the value predicted based on the law of corresponding states with the inert gases (40 K).⁵

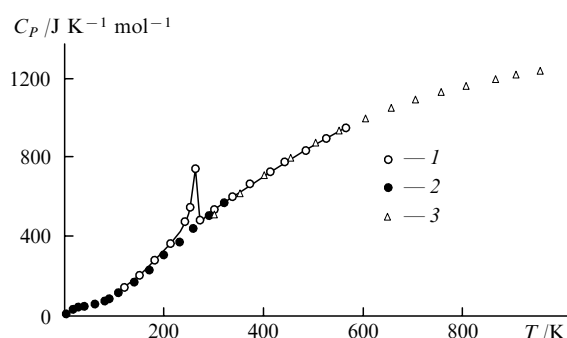


Figure 1. The heat capacity of the C₆₀ fullerene vs. temperature. (1) the DSC data;⁵³ (2) the AdC smoothed data;⁷ (3) our calculations.

In a recent paper,¹³ the data reported on the heat capacity^{65–67} and thermodynamics of phase transitions^{12,68} in C₇₀ were compared and commented. We are also aware of reports^{69–72} the results of which require no revision.¹³ The phase state of C₇₀ fullerene is influenced by the sample prehistory.^{73–79} A crystal I in the high-temperature phase characterised by an isotropic molecular rotation can form either a hexagonal or a face-centred lattice. With time, it transforms to a crystal having a face-centred lattice which however comprises 10%–20% of a hexagonal phase. Upon cooling, the crystal I converts to the crystal II characterised by partially frozen rotational degrees of freedom and having either a rhombohedral or a distorted hexagonal ($c/a = 1.82$) structure with considerable admixture of hexagonal or rhombohedral phases, respectively. Upon further cooling, a monoclinic phase III arises which, unlike the low-temperature C₆₀ fullerene crystal, does not undergo transition to the vitreous state. At increased pressure, the transition to the phase III splits into two phase transitions. Some researchers report that the double peak on the heat capacity curve is observed also at atmospheric pressure and explain this phenomenon by either a mixture of the crystal phases present in a sample or successively proceeding phase transitions. It might be suggested from the aforesaid that two modifications of the low-temperature monoclinic crystal are available and the residual entropy of C₇₀ is not zero at 0 K. Unfortunately, the latter could not be estimated. Note that according to Ref. 13, the transformation of the crystal III to II (Table 7) is associated with one peak on the heat capacity curve.

We calculated the thermodynamic parameters of solid C₇₀ in the range 0–340 K (Table 8) based on the heat capacities measured by AdC.¹³ To our knowledge, the report¹³ is the only one which gives the numerical values of heat capacities of C₇₀ in this temperature range. In the range 340–560 K, we used the heat capacities measured by DSC.^{13,65} The heat capacity of C₇₀ was earlier extended to $T = 1000 K$ (see Refs 26 and 65); we made an extension by a procedure identical to that for C₆₀. The contribution of intramolecular vibrations was calculated using the same set of frequencies as that accepted for the calculation of the thermodynamic properties in the ideal gas state (see Section VI). The translational contribution of the lattice heat capacity was accepted to be $3R$, the librational one was calculated for the hindered rotation of the C₇₀ molecules using the harmonic potential. To give the calculated heat capacity the best fit to its measured values in the range 300–560 K, the effective potential barrier to molecular rotation was chosen to be $3 kJ mol^{-1}$. The difference $C_P - C_V$ was estimated to be $2.6 J K^{-1} mol^{-1}$ at $T = 365 K$ assuming $\alpha = 4.6 \times 10^{-5} K^{-1}$ and $\beta = 1.25 \times 10^{-10} Pa^{-1}$ (see Ref. 80). It was extended to a high-temperature region using Eqn (1). The value of k ($9.44 \times 10^{-6} K^{-1}$) was calculated from the data at 365 K.

The calculated heat capacities of crystalline C₇₀ (Fig. 2) are close to their experimental values at all the temperatures except for those around 400 K where they are $30 J K^{-1} mol^{-1}$ ($\sim 4\%$) larger than those measured by DSC.⁶⁵ In that region, the curve lies below the line connecting the adjacent regions, the reason being as yet unexplained. We estimate the error in the entropy determination of C₇₀ to be ± 3 and $\pm 15 J K^{-1} mol^{-1}$ at 298.15 and 843.5 K, respectively.

Note that in the interval 100–1000 K, excluding the phase transition areas, the heat capacities per carbon atom of the C₆₀

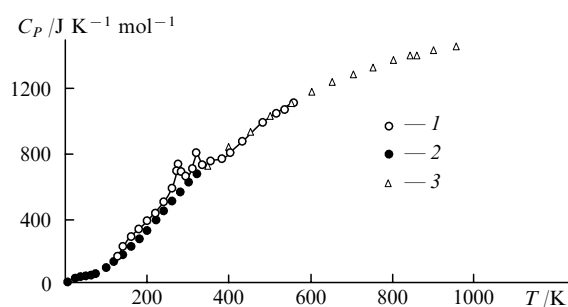
Table 7. The thermodynamic characteristics of solid-state transitions in C₇₀ (see Ref. 13).

T/K	$\Delta_{tr}H / kJ mol^{-1}$	$\Delta_{tr}S / J K^{-1} mol^{-1}$	Note
29	0.0139	0.54	non-isothermal
38	0.0176	0.47	non-isothermal
277.4	3.22	11.6	cr. III $\rightarrow$ cr. II
340	2.7±0.4	8	cr. II $\rightarrow$ cr. I

Table 8. Recommended values of the thermodynamic parameters [C_P , S and $-(G-H_0)/T$ in $\text{J K}^{-1} \text{mol}^{-1}$; $H-H_0$ in kJ mol^{-1}] of crystalline C_{70} .

T/K	C_P	S	$-(G-H_0)/T$	$H-H_0$
Crystal III				
0	0	0	0	0
5	3.71	1.17	0.274	0.00448
10	16.46	7.44	2.109	0.0533
20	34.38	25.08	9.175	0.318
50	52.77	65.74	31.92	1.691
100	105.7	114.5	60.95	5.351
150	207.1	175.4	88.52	13.04
200	337.7	252.4	119.6	26.56
250	485.4	343.4	155.0	47.10
277.40	566.9	398.1	176.3	61.52
Crystal II				
277.40	566.9	409.7	176.3	64.74
298.15	625.6	452.7	194.0	77.12
300	630.7	456.6	195.6	78.28
340	727.0	541.7	231.3	105.5
Crystal I				
340	727.0	549.6	231.3	108.2
350	746.2	571.0	240.7	115.6
400	813.0	675.0	288.6	154.6
450	940.5	777.6	337.2	198.2
500	1040	882.3	386.5	247.9
550	1116	985.0	436.3	301.8
600	1186	1085	486.2	359.4
650	1247	1183	536.0	420.2
700	1300	1277	585.6	483.9
750	1346	1368	634.7	550.1
800	1386	1456	683.4	618.5
843.5	1417	1531	725.2	679.5
850	1421	1542	731.4	688.7
900	1451	1624	778.7	760.5
950	1478	1703	825.2	833.8
1000	1502	1779	871.0	908.3

and C_{70} fullerenes are similar to those of graphite, although these are markedly different in the molecular composition and the crystal structure. It is noteworthy that unlike most organic substances, the temperature dependence of the heat capacities of fullerenes exhibits two inflections, which are caused by low Debye temperatures (~ 46 K and ~ 40 K for C_{60} and C_{70} , respectively) and low libration frequencies. When temperature increases from 0 to ~ 30 – 50 K, both the Debye and librational contributions to the fullerene lattice heat capacity approach their limiting values $3R$, whereas the intramolecular contributions still remain small in

**Figure 2.** The heat capacity of the C_{70} fullerene vs. temperature; (1) the DSC data;⁶⁵ (2) the AdC smoothed data;¹³ (3) our calculations.

this temperature range. In the range 30–50 K, the heat capacity remains relatively stable varying within 40–50 $\text{J K}^{-1} \text{mol}^{-1}$ (close to $6R$), which indicates that the Debye and librational contributions to the heat capacity are saturated. For most of organic substances, such a saturation occurs at higher temperatures being masked by an increasing contribution of the intramolecular vibrations.

Various computational approaches, from the Debye models with adjustable parameters^{22,56} to those based on the examination^{81,67} and integration^{53,82} of phonon spectra of crystals may give a key to a more comprehensive interpretation of the heat capacities of fullerenes in the condensed state. Both theoretical^{83–87} and experimental^{88,89} data on the fullerene lattice vibrations can be found in the literature.

V. Saturated vapour pressures and enthalpies of sublimation of fullerenes

The results of a recent extensive study by Piacente *et al.*²⁴ gave the saturated vapour pressure (P) and the enthalpy of sublimation of C_{60} measured by the Knudsen method, which is one of the most precise methods for measuring low vapour pressures. The problems of sample purity and stability (see Section II) were closely examined, and earlier publications^{23,25,90–96} were surveyed.²⁴ We are also aware of other reports.^{97–103} Most of the results are merely consistent with those by Piacente *et al.*²⁴ in order of magnitude. The methods of measurement and preparatory procedures described²⁴ suggest that the following values of saturated vapour pressure and enthalpy of sublimation are most reliable:

$$\ln P(\text{kPa}) = (19.07 \pm 0.46) - (21\,078 \pm 350)/T \quad (T = 730\text{--}990 \text{ K}),$$

$$\Delta_{\text{sub}}H_{860} = 175.3 \pm 2.9 \text{ kJ mol}^{-1}.$$

It follows from these values and the data listed in Table 5 that at $T = 860$ K and $P = 1$ bar, the experimental magnitude of entropy of C_{60} in the gaseous state amounts to $S_{860}(\text{g}) = 1481 \pm 14 \text{ J K}^{-1} \text{mol}^{-1}$. With the heat capacity of the crystal (see Section IV) and the results of statistical calculations of the heat capacity of a gas (see Section VI) taken into account, the enthalpy of sublimation of C_{60} at $T = 298.15$ K was recalculated:

$$\Delta_{\text{sub}}H^\circ = 183.7 \pm 5.1 \text{ kJ mol}^{-1}.$$

The saturated vapour pressure and enthalpy of sublimation of C_{70} were determined by Piacente *et al.* in their extended research.²⁶ In addition to the reports^{25,92–94,104} discussed in Ref. 26, we are also aware of other publications (Refs 101 and 105). The values

$$\ln P(\text{kPa}) = (19.30 \pm 0.35) - (22\,835 \pm 370)/T \quad (T = 783\text{--}904 \text{ K}),$$

$$\Delta_{\text{sub}}H_{843.5} = 189.9 \pm 3.1 \text{ kJ mol}^{-1},$$

determined for the freshly sublimed C_{70} sample²⁶ are recommended as most reliable by the same reasoning as those for C_{60} .

Based on these values and the data listed in Table 8, one can deduce that the experimental value of the entropy of C_{70} in the gaseous state amounts to $S_{843.5}(\text{g}) = 1653 \pm 16 \text{ J K}^{-1} \text{mol}^{-1}$ at $T = 843.5$ K and $P = 1$ bar. With the crystal heat capacity (see Section IV) and the results of statistical calculations of the heat capacity of a gas (see Section VI) taken into account, the enthalpy of sublimation of C_{70} at $T = 298.15$ K was recalculated to be

$$\Delta_{\text{sub}}H^\circ = 200.3 \pm 6.1 \text{ kJ mol}^{-1}.$$

VI. Thermodynamic properties of C_{60} and C_{70} in the ideal gas state

Thermodynamic properties of fullerenes in the gaseous state were calculated by the methods of statistical thermodynamics.^{6,24,26} All the calculated entropy values of C_{60} appeared to be lower than the experimental ones (see Section V). In our opinion, the most reasonable set of frequencies of normal modes was used by

Piacente *et al.*²⁴ They averaged the values measured using IR¹⁰⁶ and Raman spectroscopy,^{107–109} inelastic neutron scattering^{110,111} and those derived from the calculations of the normal modes.¹¹² It appeared that the statistical calculation carried out using the average frequencies of normal modes gives the entropy of gaseous C₆₀ which is closest to its experimental value. Schettino *et al.*¹⁰⁶ gave also a short survey of the spectroscopy and assignment of the C₆₀ vibration frequencies. Later, other reviews on IR spectroscopy of fullerenes¹¹³ and assignment of the C₆₀ vibration frequencies^{114–121} were published. To our knowledge, no contradictions exist at present as to the interpretation of the C₆₀ molecular vibration frequencies.

In the present review, the thermodynamic parameters of fullerenes in the ideal gas state were calculated as described by Frenkel *et al.*¹²² The translational contributions of C₆₀ and C₇₀ were calculated using their molecular masses equal to 720.66 and 840.77, respectively. In the calculation of rotational contributions, the symmetry numbers 60 and 10 and the products of the principal moments of inertia ($I_A I_B I_C$) equal to 1.00×10^{-129} and 2.50×10^{-129} kg³ m⁶ were used for C₆₀ and C₇₀, respectively. The two latter values were calculated by the models fairly consistent with the X-ray structural results¹²³ (for C₆₀) and the electron diffraction data¹²⁴ (for C₇₀). The scatter in the entropy values of C₆₀ in the gaseous state does not exceed 0.2 J K⁻¹ mol⁻¹, although different estimates of the moments of inertia are available in different publications. The frequencies of normal modes of C₆₀ (Table 9) were averaged over the measured values.¹⁰⁶ The contribution of the excited electronic states (assuming that all the remaining contributions are independent on the electronic state of molecules) was estimated from the relative energies of one-electron states (Table 10). According to the model used, the contribution of the excited electronic states to the heat capacity of C₆₀ at temperatures above 3000 K amounts to 5 J K⁻¹ mol⁻¹, whereas a similar contribution to the entropy is reached at 4500 K. The calculated value of S_{860}° (1463.8 J K⁻¹ mol⁻¹, Table 11) is 17 J K⁻¹ mol⁻¹ smaller than that determined experimentally (1481 ± 14 J K⁻¹ mol⁻¹). Therefore, 17 J K⁻¹ mol⁻¹ can be considered as the error in calculation of the entropy of C₆₀ in the gaseous state. This comprises ~1.5% of the vibrational contribution to the entropy, as in the case of the cage hydrocarbons C₁₁H₁₄ and C₁₄H₁₆ with rigid carbon skeletons.^{129,130} To make both the entropy of fullerenes in the gaseous state and the heat capacity of a crystal (see Section IV) consistent with the experimental data, we examined a possibility to revise the C₆₀ vibration frequencies. In order for the calculated entropy of C₆₀ in the gaseous state to be equal to its measured value, one has to reduce the wave numbers hence breaking the agreement of the calculated heat capacity of a crystal

Table 9. The frequencies of the C₆₀ normal modes used in statistical calculations.

Type	Degeneracy	Wave number /cm ⁻¹
A_g	1	491, 1458
H_g	5	266, 429, 710, 768, 1095, 1254, 1437, 1570
T_{1g}	3	565, 850, 1289
T_{2g}	3	535, 764, 805, 1334
G_g	4	484, 570, 738, 1135, 1314, 1515
A_u	1	973
T_{1u}	3	527, 578, 1184, 1439
T_{2u}	3	355, 714, 1040, 1187, 1565
H_u	5	403, 486, 669, 740, 1211, 1342, 1530
G_u	4	344, 760, 771, 967, 1321, 1415

Table 10. The low-lying excited electronic states of the C₆₀ molecule.

Type	Energy /eV				Degeneracy
	I	II	III	IV	
1 $^1T_{2g}$	2.58	2.29	1.88	1.88	3
1 $^1T_{1g}$	2.61	2.33		2.33	3
1 ^1G_g	2.70	2.34		2.34	4
1 $^1T_{2u}$	2.89	2.76		2.76	3
1 ^1H_u	3.15	3.01		3.01	5
1 ^1H_g	3.15	2.65		2.65	5
1 ^1G_u	3.21	3.11		3.11	4
2 ^1H_u	3.89	3.70		3.70	5
2 ^1G_u	3.90	3.38		3.38	4
1 $^1T_{1u}$	4.08	3.36		3.36	3
2 $^1T_{2u}$	4.12			4.12	3
3 ^1G_u	4.37			4.37	4
3 ^1H_u	4.39			4.39	5
2 $^1T_{2g}$	4.41			4.41	3
2 $^1T_{1u}$	4.51	4.00		4.00	3
3 $^1T_{1u}$	6.19	4.26		4.26	3
1 $^3T_{2g}$	2.06		1.6	1.60	3
1 $^3T_{1g}$	2.40			2.40	3
1 ^3G_u	2.58			2.58	4
1 ^3H_g	2.59			2.59	5
1 $^3T_{2u}$	2.59			2.59	3
1 $^3T_{1u}$	2.61			2.61	3
1 ^3G_g	2.66			2.66	4
1 ^3H_u	2.98			2.98	5
2 $^3T_{2u}$	3.66			3.66	3
2 ^3H_u	3.81			3.81	5
2 ^3G_u	3.84			3.84	4
2 ^3G_g	4.26			4.26	4
2 ^3H_g	4.28			4.28	5
3 ^3G_u	4.29			4.29	4
2 $^3T_{2g}$	4.32			4.32	3
3 ^3H_u	4.32			4.32	5
3 $^3T_{1u}$	4.34			4.34	3

Note. I, see Ref. 125; II, see Ref. 126; III, see Refs 127 and 128; IV, the energies used in the calculations of contributions of the excited electronic states to the thermodynamic parameters (Table 11).

with the experiment. Therefore, the agreement currently available between the thermodynamic and molecular data on the C₆₀ fullerenes seems to be the best at present.

The set of frequencies of the C₇₀ normal modes (Table 12) was obtained by averaging the experimental values (the IR^{114,131,132} and Raman^{114,131} spectroscopic data) based on the reported frequency assignment^{133,134} (see Ref. 26). The report¹³³ was followed by publication of the data¹¹³ on IR spectroscopy of fullerenes and assignments of frequencies of the C₇₀ normal modes^{115,117,118,121} which require no revision.^{133,134}

The calculated value of $S_{843.5}^\circ$ (1669.2 J K⁻¹ mol⁻¹) is 16 J K⁻¹ mol⁻¹ larger than the experimental one (1653 ± 16 J K⁻¹ mol⁻¹). This difference can be considered as the uncertainty in the calculated entropy of C₇₀ in the gaseous state. Unfortunately, we have no information on a reasonably complete set of the excited electronic state energies for the C₇₀ molecule. The experiments^{127,135} provide evidence that the low-lying electronically excited states are expected to have slightly lower energies than those of C₆₀. Nevertheless, it is believed that only at temperatures above 3000 K does the neglect of the excited electronic state contributions increase significantly the error in the calculation of the entropy of C₇₀ in the gaseous state.

Table 11. The thermodynamic properties of the C₆₀ and C₇₀ fullerenes [S° , C_p° , $(H-H_0)/T$ and $-(G-H_0)/T$ in J K⁻¹ mol⁻¹; $\Delta_f H^\circ$ and $\Delta_f G^\circ$ in kJ mol⁻¹] in the ideal gas state at 101 325 Pa.

T/K	S°	C_p°	$\frac{H-H_0}{T}$	$-\frac{G-H_0}{T}$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
Fullerene C ₆₀						
0	0	0	0	0	2534.6	2538.6
50	254.7	34.8	33.4	221.2	2535.8	2527.8
100	286.9	72.3	41.0	245.9	2535.2	2516.2
150	331.6	160.2	65.1	266.6	2533.6	2505.0
200	392.7	272.0	102.6	290.2	2532.0	2494.4
273.15	502.8	442.3	170.8	331.9	2530.4	2479.5
298.15	543.9	498.5	196.0	348.0	2530.0	2474.5
300	547.0	502.6	197.8	349.2	2530.0	2474.2
400	720.4	706.3	300.3	420.1	2529.4	2454.3
500	896.4	870.2	398.6	497.8	2528.9	2434.6
600	1066.7	996.1	488.1	578.6	2527.8	2415.0
700	1227.8	1091.3	567.8	659.9	2526.1	2395.7
800	1378.4	1163.3	638.0	740.4	2523.7	2376.6
860	1463.8	1198.0	675.9	787.9	2522.0	2365.3
900	1518.7	1218.3	699.5	819.2	2520.8	2357.9
1000	1649.4	1260.9	753.6	895.8	2517.5	2339.6
1100	1771.2	1294.3	801.3	969.9	2513.7	2321.6
1200	1885.0	1320.9	843.6	1041.5	2509.4	2304.0
1300	1991.6	1342.3	881.1	1110.5	2505.0	2287.0
1400	2091.7	1359.8	914.7	1177.0	2499.4	2269.5
1500	2186.1	1374.2	944.9	1241.2	2493.5	2252.8
1750	2400.0	1400.9	1008.3	1391.8	2477.1	2214.0
2000	2588.4	1418.9	1058.5	1529.8	2456.7	2176.9
2500	2907.6	1441.5	1133.1	1774.6	2406.5	2110.7
3000	3171.8	1456.2	1185.8	1986.1	2350.4	2058.1
3500	3397.2	1468.8	1225.3	2171.9	2266.0	2008.3
4000	3594.2	1481.3	1256.5	2337.7	2172.9	1968.1
4500	3769.4	1493.6	1282.2	2487.2	2086.0	1964.7
5000	3927.3	1504.2	1303.9	2623.4	1970.0	1943.1
Fullerene C ₇₀						
0	0	0	0	0	2760.4	2760.4
50	275.6	36.4	33.7	241.9	2761.5	2748.6
100	312.5	86.2	44.9	267.6	2760.8	2736.2
150	365.4	188.3	74.5	290.8	2759.0	2724.3
200	436.9	317.7	118.8	318.1	2757.2	2712.9
273.15	556.6	518.3	199.0	366.6	2755.3	2697.1
298.15	613.9	585.1	228.5	385.3	2755.0	2691.8
300	617.5	589.9	230.8	386.7	2755.0	2691.4
400	821.4	831.9	351.7	469.7	2754.9	2670.3
500	1028.7	1025.4	467.9	560.8	2755.3	2649.1
600	1229.4	1172.8	573.7	655.7	2755.0	2627.8
700	1418.9	1283.5	667.6	751.3	2754.0	2606.7
800	1596.0	1366.9	750.0	845.9	2752.3	2585.8
843.5	1669.1	1396.6	782.6	886.5	2751.3	2576.8
900	1760.8	1430.4	822.3	938.5	2749.8	2565.1
1000	1914.1	1479.3	885.6	1028.5	2746.8	2544.8
1100	2057.0	1517.7	941.4	1115.6	2743.2	2524.7
1200	2190.4	1548.1	990.7	1199.7	2739.0	2505.1
1300	2315.3	1572.6	1034.6	1280.7	2734.4	2486.2
1400	2432.6	1592.6	1073.8	1358.9	2728.6	2466.5
1500	2543.1	1609.1	1108.9	1434.2	2722.3	2447.8
1750	2793.6	1639.4	1182.7	1610.9	2704.5	2404.2
2000	3013.9	1659.7	1241.1	1772.8	2681.8	2362.5
2500	3387.2	1684.2	1327.6	2059.6	2625.1	2287.9
3000	3695.5	1697.8	1388.2	2307.3	2560.0	2229.0
3500	3957.9	1706.1	1433.1	2524.8	2459.5	2173.6
4000	4186.1	1711.5	1467.6	2718.5	2344.9	2129.7
4500	4387.9	1715.2	1494.9	2893.0	2232.6	2130.0
5000	4568.8	1717.9	1517.1	3051.7	2081.1	2110.4

Table 12. The frequencies of the C₇₀ normal modes used in statistical calculations.

Type	Degeneracy	Wave number /cm ⁻¹
A'_1	1	258, 357, 457, 573, 678, 728, 1061, 1175, 1189, 1363, 1433, 1522
A'_2	1	501, 550, 651, 742, 817, 958, 1208, 1325, 1432
E'_1	2	310, 341, 424, 509, 535, 578, 642, 683, 750, 792, 820, 904, 1073, 1135, 1222, 1254, 1280, 1318, 1384, 1454, 1569
E'_2	2	227, 305, 426, 491, 519, 643, 697, 711, 728, 765, 785, 792, 933, 1069, 1164, 1224, 1280, 1314, 1336, 1452, 1496, 1570
A''_1	1	333, 545, 612, 768, 807, 917, 1223, 1322, 1536
A''_2	1	322, 458, 566, 716, 843, 1099, 1179, 1292, 1414, 1501
E''_1	2	232, 409, 479, 505, 537, 665, 703, 739, 771, 793, 1050, 1088, 1186, 1259, 1298, 1332, 1377, 1470, 1515
E''_2	2	300, 384, 471, 588, 641, 690, 738, 748, 780, 800, 988, 1062, 1143, 1231, 1301, 1328, 1384, 1442, 1500, 1548

VII. Conclusion

Based on the analysis of the published data, the values of the most important thermodynamic parameters are recommended for the C₆₀ and C₇₀ fullerenes in the crystalline state in the temperature range 0–1000 K and in the gaseous state in the range 100–5000 K. We believe that their further refinement will be made within the limits of error outlined in the present review.

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^b — *Russ. Chem. Bull. (Engl. Transl.)*

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Alkenyliodonium salts

N Sh Pirkuliev, V K Brel, N S Zefirov

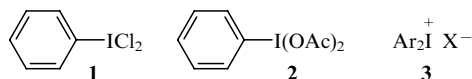
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Abstract. New data on the synthesis and chemical transformations of alkenyliodonium salts are summarised and analysed. The bibliography includes 146 references.

I. Introduction

The first synthesis of a three-coordinated iodine with at least one C–I bond was reported by Willgerodt in 1886.¹ Following preparation of (dichloro- λ^3 -iodanyl)benzene[†] (**1**) by chlorination of iodobenzene, Willgerodt soon synthesised (diacetoxy- λ^3 -iodanyl)benzene (**2**) and other organic derivatives of three- and poly-coordinated iodine. By the time of the publication by Willgerodt in 1914 of his comprehensive treatise² on the chemistry of hypervalent iodine that summarised the data on the synthesis of tri- and pentavalent iodine-containing organic compounds, about 500 such compounds were already known. Among them, diaryliodonium salts **3** were examined most thoroughly.



The chemistry of organic compounds of polyvalent iodine was the subject of several reviews (see, for example, Refs 3–5). However, because of rapid development of this chemistry, it is nearly impossible at the moment to consider all its aspects in the framework of only one publication.

A brief review⁶ has been published on iodonium salts; they were also considered in a chapter of a monograph⁷ devoted to organic compounds of polyvalent iodine. The chemistry of

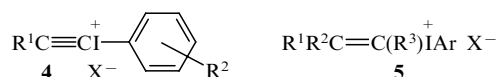
diacyloxyiodanylarenes was treated in a special review⁸ and the application of these compounds as oxidising reagents is described in a monograph.⁹ A review¹⁰ devoted to the use of compounds of polyvalent iodine, mostly organic compounds, has also been published. Interesting data on the chemistry of iodonium salts can be found in the book ‘The Problems of Organic Chemistry’^{11,12} and those on the chemistry of diacyloxyiodanylarenes in two other books;^{13,14} derivatives of iodosylarenes are discussed in a separate review.¹⁵

Organic compounds of three- and poly-coordinated iodine are widely used as reagents in modern organic chemistry. Particular areas of synthetic application of these compounds vary depending on their structures, *viz.*, on the number of organic ligands at the iodine atom^{4,7} and on the electronegativity and nucleofugality of their heteroatomic ligands.

All compounds of polyvalent iodine can be conventionally divided into several groups. The first one comprises compounds with one carbon ligand (RIX₂ and RIX₄), *viz.*, hydroxy(sulfonyloxy)- λ^3 -iodanylarenes, periodinanes, substituted benzoiodoxols and azides of trivalent iodine.^{8,10,16–30} Compounds of this group are employed for selective oxidation of various organic substrates. The second group of polyvalent iodine compounds includes iodonium salts R₂I⁺X[–] with two carbon ligands.^{8,10,16–30} Iodonium salts do not possess strong oxidising properties and are mainly employed as precursors of nucleophilic species resulting from transformations of an organic ligand.

Depending on the nature of the organic ligand R, iodonium salts, in turn, can be conventionally classified as alkyl-, polyfluoroalkyl-, alkenyl- and alkynyl-iodonium salts. Most of alkyl-iodonium salts Alk₂I⁺X[–] or Alk(Ph)I⁺X[–], with a few exceptions,³¹ are unstable and therefore have not been exploited in organic synthesis. On the contrary, polyfluoroalkyliodonium salts R_f(Ph)I⁺X[–] are stable and represent effective electrophilic polyfluoroalkylating reagents.³² Compounds of three-coordinated iodine with three organic ligands are, as a rule, unstable at room temperature; only a few stable representatives of this class are known to date.^{33–35}

Derivatives of the type **4** containing an alkynyl group as a substituent were unknown until recently. The intense development of the chemistry of alkenyliodonium salts **5** began only recently, although the first representative of this class of compounds was described back in 1914.²



At the moment, synthetic aspects of the chemistry of alkynyl-iodonium salts are well developed and discussed in detail, for

[†] This naming is given in accord with IUPAC Nomenclature of Organic Compounds (Recommendations 1993). Furthermore, symbol λ^3 can be omitted from the names of iodine-containing compounds.

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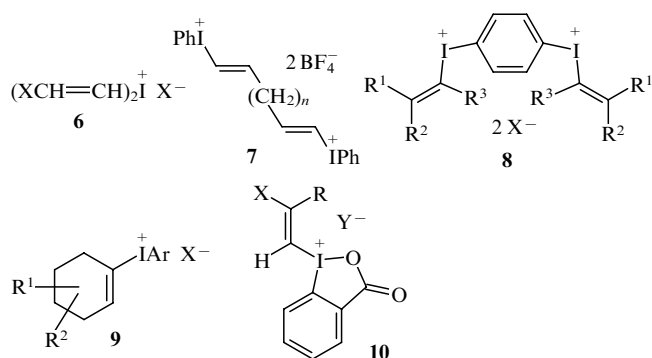
example, in monographs^{36–38} and reviews^{25,39,40} One of these reviews²⁵ contains a section treating the chemistry of alkenyliodonium salts. This chemistry was also briefly considered in another review⁴¹ devoted to organic compounds of polyvalent iodine. However, new important results obtained recently in this field deserve generalisation.

It is the purpose of this review to systematise and analyse the data on the synthesis and properties of alkenyliodonium salts which were mainly published over the last 10–15 years. Earlier publications are cited only as may be necessary for the better elucidation of the issues in question.

II. Synthesis of alkenyliodonium salts

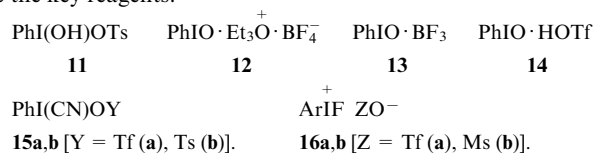
In recent decades, the interest in alkenyliodonium salts has sharply increased. Alkenyliodonium salts bearing not only alkyl, but also aryl, triflate, mesylate and other substituents at the double bond were synthesised. These compounds were demonstrated to be very promising intermediates for organic synthesis.

At present, several types of alkenyliodonium salts are known, viz., those with one (**5**) or two (**6–8**) alkenyl groups and also cyclic alkenyliodonium salts of the type **9** and **10**.



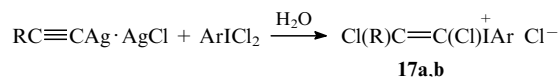
Several methods for the synthesis of alkenyliodonium salts have been described earlier.⁷ However, none of them has been really convenient until recently. At present, a number of new methods have been developed, however, these did not receive much attention in relevant reviews.^{25,41} Taking this fact into account, we systematise in this Section the published data on the synthesis of alkenyliodonium salts.

These syntheses are based on the use of electrophilic λ^3 -iodanes. Among compounds of polyvalent iodine, the Koser reagent **11**, complexes of iodosylbenzene **12** and **13**, alkynyliodonium salts **4**, the iodosylbenzene trifluoromethanesulfonic acid complex **14**, cyano(hydroxy)- λ^3 -iodanylbenzene triflate and tosylate (**15a,b**), fluoro(hydroxy)- λ^3 -iodanylbenzene sulfonates (**16a,b**) are the key reagents.



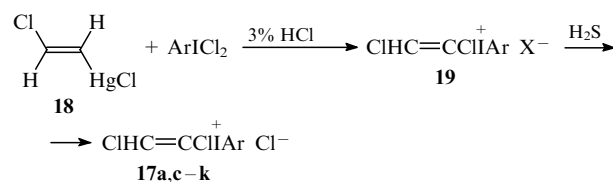
1. Syntheses starting from dichloro- λ^3 -iodanylbenzene and dichloro- λ^3 -iodanylalkenes

Early methods for the synthesis of alkenyliodonium salts were based on the reactions of organometallic derivatives of alkynes with dichloroiodanylarenes. Using this approach, alkenyliodonium salts **17a,b** have been synthesised.² However, on the whole, this method was rather ineffective and had a number of limitations.



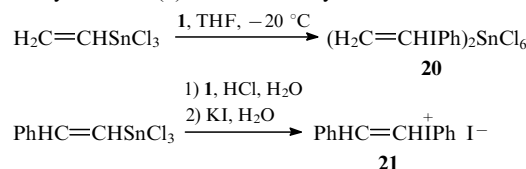
R = H, Ar = Ph (**17a**); R = Me, Ar = C₆H₄Me-2 (**17b**).

Later, the reactions of organomercuric derivatives of alkenes with dichloroiodanylarenes were proposed to synthesise alkenyliodonium salts.^{42–44} Thus the treatment of *trans*-chlorovinylmercuric chloride with various dichloroiodanylarenes in dilute hydrochloric acid results in arylvinyliodonium mercurates **19** in 5%–53% yields. The latter can be converted into the corresponding arylvinyliodonium chlorides **17a,c–k** upon treatment with hydrogen sulfide.

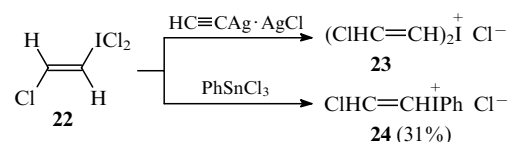


Ar = Ph (**a**), 2-MeC₆H₄ (**c**), 3-MeC₆H₄ (**d**), 4-MeC₆H₄ (**e**), 2-ClC₆H₄ (**f**), 3-ClC₆H₄ (**g**), 4-ClC₆H₄ (**h**), 2-MeOC₆H₄ (**i**), 4-MeOC₆H₄ (**j**), 3-NO₂C₆H₄ (**k**); X = Cl·HgCl₂, Cl·2 HgCl₂.

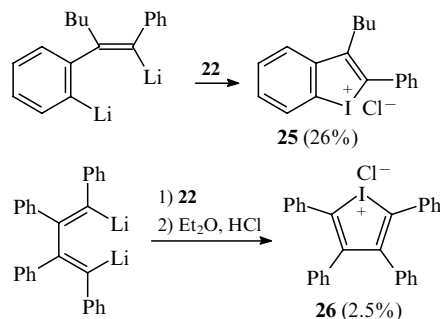
The reaction of vinyl- or styryltrichlorostannane with dichloroiodanylbenzene (**1**) leads to alkenyliodonium salts **20** or **21**.^{45,46}



1-Chloro-2-dichloroiodanylethylene **22** has been synthesised for the first time by the reaction of *trans*-chloroiodoethylene with chlorine.⁴⁷ Later, compound **22** was obtained in high yield by the reaction of acetylene with iodine trichloride.⁴⁸ Compound **22** is unstable at room temperature, but can be stored below –20 °C for two months without noticeable changes. This reagent is employed for the synthesis of alkenyliodonium salts. Thus its reactions with silver acetylide or phenyltrichlorostannane afford compounds **23** and **24**.⁴⁶



Diphenyliodonium chloride rather than a vinylidonium salt of the type **24** is formed from 1-dichloroiodanyl-2-iodoethylene in 50% yield.⁴³ Organolithium derivatives react with compound **22** to give cyclic iodonium salts **25** and **26**.⁴⁹

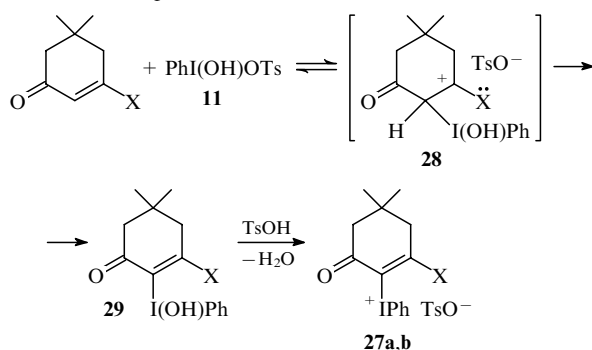


It should be noted that the reaction of dichloroiodanylbenzene with an equivalent amount of vinylolithium in THF at –70 °C affords diphenyliodonium chloride in low yield (5%).⁴⁹

2. Syntheses starting from dihydroxy- λ^3 -iodanylbenzene tosylate

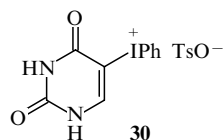
The availability of iodanylbenzene derivatives, their reasonable stabilities on storage and fair solubilities enable the use of these compounds in the synthesis of alkenyliodonium salts. The reac-

tions of dihydroxy- λ^3 -iodanylbenzene tosylate (**11**) with 3-amino- and 3-ethoxy-5,5-dimethylcyclohex-2-enone in chloroform result in the formation of vinyliodonium salts **27a,b** in 87% and 40% yields, respectively.⁵⁰ The reaction mechanism presumably involves the initial attack by the hydroxy(phenyl)iodonium ion on the double bond followed by the deprotonation of the intermediate **28** and the exchange reaction of aryl(vinyl)iodonium hydroxide **29** with *p*-toluenesulfonic acid.

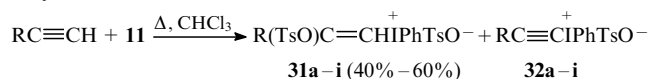


X = NH₂ (**a**), OEt (**b**).

The condensation of uracil with diacetoxyiodanylbenzene in DMF in the presence of TsOH · H₂O leads to compound **30** in 78% yield.⁵¹ The reaction apparently involves the intermediate formation of the tosylate **11**.



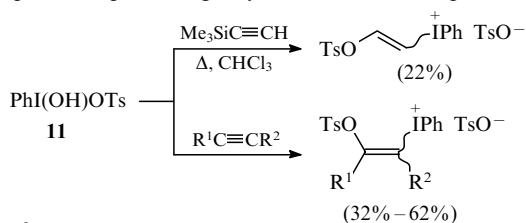
More general and simple procedure for the synthesis of (β-tosyloxyvinyl)iodonium tosylate **31** includes the reactions of dihydroxyiodanylbenzene tosylate (**11**) with terminal alkynes.^{52–56}



R = Prⁿ (**a**), Buⁿ (**b**), n-C₅H₁₁ (**c**), Prⁱ (**d**), sec-C₄H₉ (**e**), Buⁱ (**f**), cyclo-C₆H₁₁ (**g**), Bu^t (**h**), Ph (**i**).

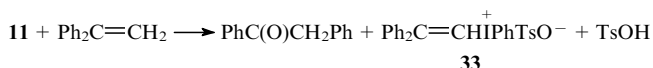
Depending on the nature of the substituent in terminal alkynes, either alkenyl- or alkynyliodonium salts or their mixture are formed.⁵⁴ Thus pent-1-yne yields the alkenyliodonium salt **31a** exclusively (58%), 3,3-dimethylbut-1-yne gives alkynyliodonium tosylate **32h** (74%), while 3-methylbut-1-yne affords a mixture of alkenyl- (**31d**) (11%) and alkynyl-iodonium salts **32d** (15%). A correlation was found between the degree of branching in the substituent and the direction of the reactions. Thus alkynyliodonium salts are formed if the substituent is more branched than the isopropyl group (*e.g.*, Bu^t and cyclo-C₆H₁₁). Mixtures of both salts are obtained from 3-methylbut-1-yne and 4-methylpent-1-yne, which are branched in the β-position.

Trimethylsilylacetylene reacts with compound **11** with the elimination of the trimethylsilyl group to give phenyl(2-tosyloxyvinyl)iodonium tosylate.⁵⁴ Disubstituted acetylenes react with compound **11** producing vinyliodonium salts in up to 62% yield.⁵³

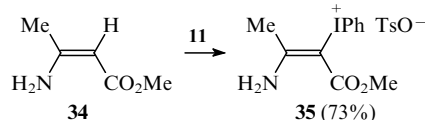


R¹, R² = Me, Buⁿ, n-C₅H₁₁, Ph.

The reactions of compound **11** with alkenes were also studied.⁵³ Alkenyliodonium salt **33** (5%) was found to be a product of the reaction with 1,1-diphenylethylene.

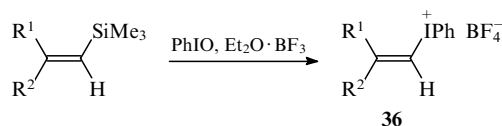


Methyl 3-aminocrotonate **34** reacts with the tosylate **11** at 20 °C to give [2-amino-1-methoxycarbonyl-(*E*)-prop-1-enyl]phenyliodonium tosylate (**35**) as the major product.⁵⁷



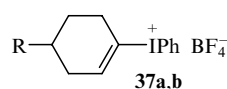
3. Syntheses starting from iodosylbenzene in the presence of Lewis acids

The first general method for the synthesis of alkenyliodonium salts was suggested in the mid-1980s.^{58, 59} It was based on the reactions of silylated alkenes with iodosylbenzene in the presence of Lewis acids. These reactions proceed stereoselectively in the presence of boron trifluoride diethyl etherate to afford alkenyliodonium tetrafluoroborates **36** in high yields. The preparation of a wide range of diverse alkenyliodonium salts has demonstrated the versatility of this procedure. The yields of the reaction products reached 89%.



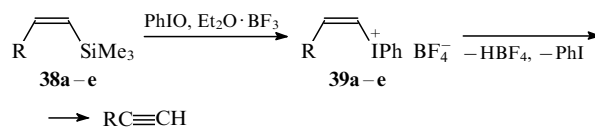
R¹ = H, Me, n-C₈H₁₇, Ph(CH₂)₂; R² = H, Me, n-C₈H₁₇, Ph, PhCH₂, Ph(CH₂)₂, *p*-BrC₆H₄OCH₂, *p*-ClC₆H₄(CH₂)₂.

Using this approach, cyclic alkenyliodonium salts, *viz.*, 4-*R*-cyclohex-1-enyl(phenyl)iodonium tetrafluoroborates **37a,b**, were synthesised.^{58, 59}



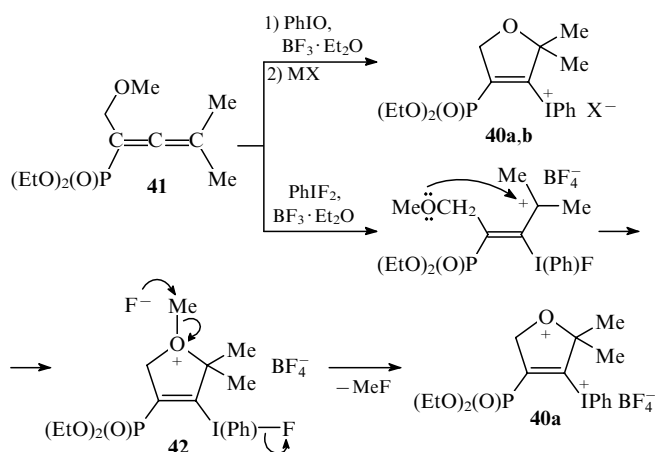
R = H (**a**), Bu^t (**b**).

The reaction of 1-trimethylsilyldec-1-ene with iodosylbenzene in the presence of boron trifluoride diethyl etherate yields dec-1-yne.^{60, 61} Using NMR spectroscopy, it was shown that the reaction with the alkene **38a** occurs *via* unstable alkenyl(phenyl)iodonium salt **39a**.⁵⁸ Treatment of salts **39a–e** with an aqueous solution of KClO₄ allowed the synthesis and characterisation of stable (*Z*)-alkenyliodonium perchlorates **39a–e**.⁶¹



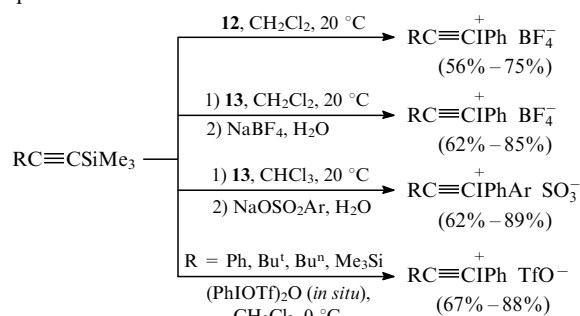
R = n-C₈H₁₇ (**a**), Me₂CH(CH₂)₄ (**b**), cyclo-C₅H₉CH₂ (**c**), Ph (**d**), Ph(CH₂)₃ (**e**).

Electrophilic addition of the complex of PhIO with BF₃ · Et₂O to allenes was used to synthesise alkenyliodonium salts. Thus salt **40a** was obtained by the reaction of diethyl 1-methoxy-4-methylpenta-2,3-dien-2-ylphosphonate (**41**) with 2 equivs of iodosylbenzene in the presence of boron trifluoride diethyl etherate.⁶² The respective perchlorate **40b** was obtained in 48% yield upon treatment of the reaction mixture with a saturated aqueous solution of LiClO₄. The salt **40** is also formed in the reaction of the allene **41** with a system PhIF₂ – BF₃ · Et₂O.⁶²


$$X = \text{BF}_4 \text{ (a)}, \text{ClO}_4 \text{ (b)}.$$

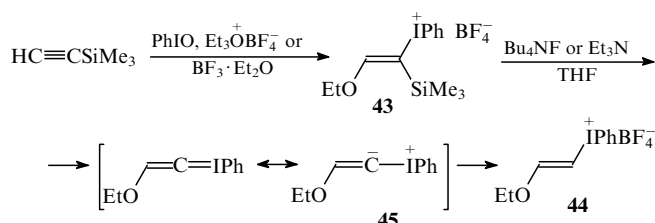
The unusual reaction course is explained by a *Z*-orientation of the electrophilic fragment I(Ph)F relative to the phosphoryl group in the intermediate **42**. In all the structures examined so far,^{63–71} resulting from electrophilic additions to allenylphosphonates, *E*-orientation of the substituents at the double bond was mainly observed, which favoured the formation of oxaphospholenes.

The reactions of alkynyltrimethylsilanes with iodosylbenzene in the presence of BF_3 or $\text{Et}_3\text{O}^+ \cdot \text{BF}_4^-$ lead to alkynyliodonium compounds.⁷²⁻⁷⁷



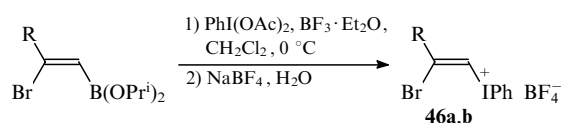
R = Ph, PhCH₂, PhCH₂CH₂, n-C₈H₁₇, cyclo-C₆H₁₁;
Ar = 4-MeC₆H₄, 4-NO₂C₆H₄.

The addition of PhIO to trimethylsilylacetylene in the presence of triethyloxonium tetrafluoroborate or boron trifluoride diethyl etherate results in the formation of (*E*)-(2-ethoxyvinyl-1-trimethylsilyl)phenyliodonium tetrafluoroborate in 68% yield.⁷⁸ Treatment of compound **43** with tetra-*n*-butylammonium fluoride or triethylamine leads to vinylidonium salt **44**. The reaction presumably occurs *via* an intermediate ylide **45**.⁷⁸



A method allowing the stereoselective synthesis of alkenyliodonium salts from boronic acids or their esters has been described.⁷⁹ The reactions of (*Z*)-2-bromovinyl(diisopropoxy)-boranes with diacetoxyiodanylbenzene in dichloromethane at 0 °C under nitrogen followed by the anion exchange led to (*Z*)-phenyl(vinyl)iodonium tetrafluoroborates. In addition to the iodonium salt **46b**, (*Z*)-2-bromodec-2-enal (9%), 2,2-dibromodec-1-enal (3%) and (*Z*)-1,2-dibromodec-1-ene (5%) were also formed.

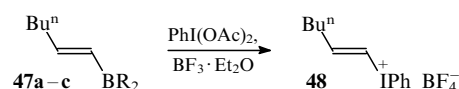
If the reactions are carried out in the presence of boron trifluoride etherate, the yields of alkenyliodonium salts are increased to 85%.


$$R = \text{Bu}^n \text{ (a)}, n\text{-C}_8\text{H}_{17} \text{ (b)}.$$

The yields of the salts **46** also depend on the nature of the solvent; in dichloromethane, benzene, ethyl acetate and methanol, they are higher (> 80%) than in acetonitrile and diethyl ether.

Alkoxyboranes also produce alkenyliodonium salts in reactions with other derivatives of I(III), *viz.*, with PhIO in the presence of boron trifluoride etherate, dihydroxyiodanylbenzene tosylate (**11**) or PhI(OCOCF₃)₂.⁷⁹ When (*Z*)-2-bromohex-1-enyl(diisopropoxy)borane reacted with bis(trifluoroacetoxy)iodanylbenzene, [(*Z*)-2-bromohex-1-enyl]phenyliodonium trifluoroacetate was isolated from the reaction mixture together with the respective tetrafluoroborate as the major product.

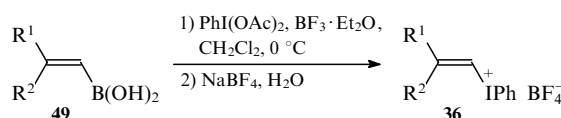
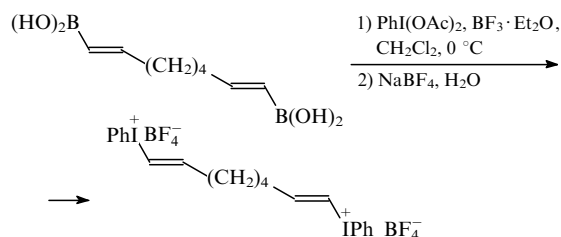
The reaction of (*E*)-(diisopropoxy)hex-1-enylborane (**47a**) with $\text{PhI}(\text{OAc})_2 - \text{BF}_3 \cdot \text{Et}_2\text{O}$ results in the stereoselective formation of (*E*)-vinyliodonium salt **48** (47%) and hexenal as a side-product (12%).


$$R_2 = (\text{OPr}^i)_2 \text{ (a)}, -\text{OCMe}_2\text{CMe}_2\text{O}- \text{ (b)},$$



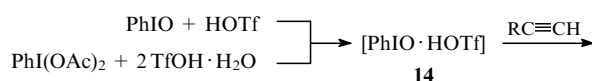
(c).

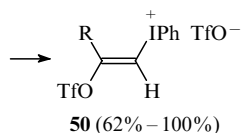
Vinylboronic acids **49** react with $\text{PhI}(\text{OAc})_2 - \text{BF}_3 \cdot \text{Et}_2\text{O}$ in dichloromethane at 0 °C under nitrogen to form vinyliodonium salts **36**.⁷⁹ This procedure allows the synthesis of not only mono-, but also bis(vinyliodonium) salts from the corresponding vinylboronic acids.⁷⁹


$$R^1 = n\text{-C}_4\text{H}_9, n\text{-C}_8\text{H}_{17}, \text{Ph}(\text{CH}_2)_3, \text{Cl}(\text{CH}_2)_3, \text{NC}(\text{CH}_2)_3, \\ \text{cyclo-C}_5\text{H}_9\text{CH}_2, \text{Me}_2\text{CH}(\text{CH}_2)_2, \text{Bu}^t, \text{Ph}; R^2 = \text{H}, \text{Me}, \text{Ph}.$$


4. Syntheses based on the activation of iodosylbenzene with trifluoromethanesulfonic acid or its derivatives

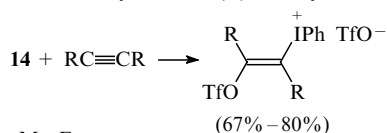
Yet another method for the synthesis of alkenyliodonium salts is based on the reactions of alkynes with PhIO–HOTf (**14**), PhIO–Tf₂O or PhIO–Me₃SiOTf systems.^{80–82} These reactions occur stereoselectively yielding (*E*)-alkenyliodonium salts **50**. Complex **14** is generated *in situ* either from a 1:1 mixture of iodosylbenzene and trifluoromethanesulfonic acid or from a 1:2 mixture of diacetoxyiodanylbenzene and TFOH·H₂O.





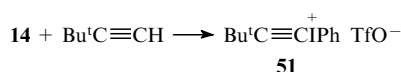
R = H, Prⁿ, Buⁿ, n-C₆H₁₃, Ph.

Disubstituted acetylenes also react with the complex **14** stereoselectively to form (*E*)-alkenyliodonium salts.⁸²

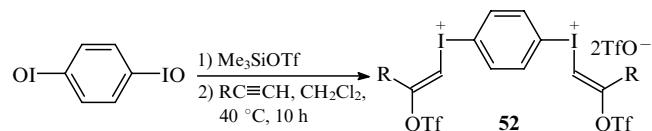


R = Me, Et.

However, only alkynyliodonium triflate **51** is formed in 42% yield in the reaction of sterically hindered 3,3-dimethylbut-1-yne with PhIO–HOTf.⁸²

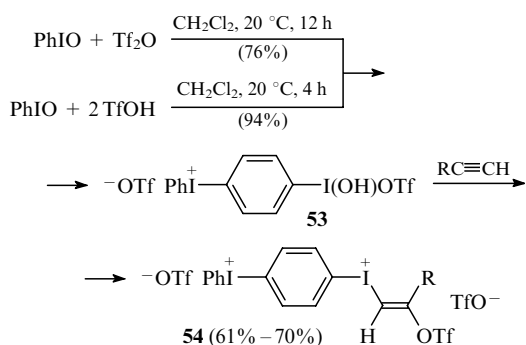


Activation of bis(iodosyl)benzene with trimethylsilyl triflate followed by treatment with appropriate terminal alkynes afford bis(alkenyliodonium) salts **52** in 50%–66% yields.⁸³



R = H, Me, Et, Ph.

The reaction of iodosylbenzene with 2 equivs of trifluoromethanesulfonic acid or with an equimolar amount of Tf₂O produces the iodanyl-iodonium derivative **53**. The latter readily reacts with terminal alkynes to give the corresponding *E*-alkenyliodonium salts **54**.^{84, 85}

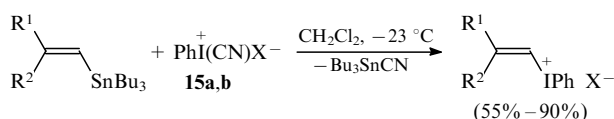


R = Prⁿ, Buⁿ, n-C₆H₁₃.

It should be noted that 1-trimethylsilylalkynes react with the reagent **53** with the elimination of the trimethylsilyl group to form the corresponding mono(alkynyl)iodonium salts.⁸⁵

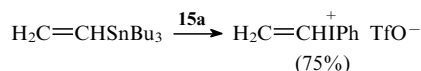
5. Syntheses starting from cyano(hydroxy)-λ³-iodanylbenzene triflate

A more versatile method for the synthesis of alkenyliodonium salts that allows the introduction of a wide range of different substituents at the double bond is based on the reactions of cyano(hydroxy)-λ³-iodanylbenzene sulfonates **15a,b** with tin-substituted alkenes.^{86–88}



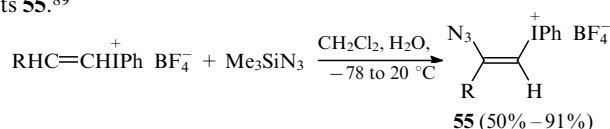
R¹, R² = Me, Buⁿ, Et, Ph; X = OTf (a), OTs (b).

The reactions proceed under mild conditions and stereoselectively afford alkenyliodonium salts in high yields. Using this approach, phenyl(vinyl)iodonium triflate was synthesised starting from tributyl(vinyl)stannane.⁸⁸



6. Syntheses starting from alkynyliodonium salts

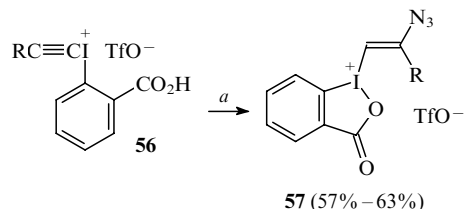
The reactions of alkynyliodonium salts with nucleophiles in protic solvents represent a convenient approach to stereoselective synthesis of (*Z*)-β-functionalised alkenyliodonium salts. The ratio between the substitution and addition products depends on the nature of the counterion and nucleophile. When trimethylsilyl azide is used as a source of nucleophilic species (in the presence of water), the addition products are formed in high yields, and it is employed for the preparation of (*Z*)-(β-azidoalkenyl)iodonium salts **55**.⁸⁹



R = Me, Bu^t, n-C₈H₁₇, cyclo-C₅H₉CH₂.

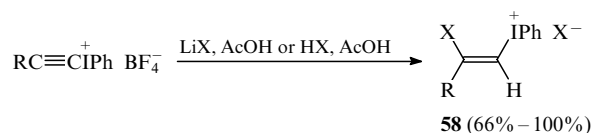
However, the reactions of alkynyliodonium tosylates with sodium azide in the presence of methanol result in the corresponding (*Z*)-(β-azidoalkenyl)iodonium tosylates in relatively low yields.⁹⁰

1-(*Z*)-(β-Azidovinyl)-3*H*-2,1λ³-benzooxaionol-3-one triflates **57** have been obtained by the reactions of alkynyliodonium salts **56** with sodium azide in the presence of 18-crown-6.⁹¹ The initial intramolecular hydrogen transfer followed by cyclisation involving the *ortho*-carboxy group may account for such unusual stereochemistry of the azide addition.



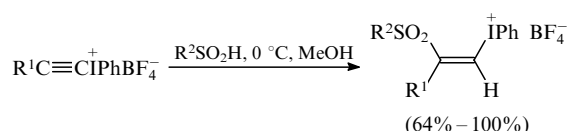
R = Buⁿ, n-C₆H₁₃, n-C₈H₁₇, n-C₁₀H₂₁;
(a) NaN₃, 18-C-6, CH₂Cl₂, –80 to 20 °C.

Stereoselective synthesis of (*Z*)-(β-halogenovinyl)iodonium salts **58** by the reactions of alkynyliodonium tetrafluoroborates with halide anions in an acid medium has been effected.^{92, 93} Fluoride anion does not react under these conditions, while the addition of iodide anion results in a complex mixture of products probably due to the low stability of the primary addition products.⁹² (*Z*)-(β-Halogenovinyl)iodonium salts **58** are useful precursors for halogenoalkylidene carbenes.⁹³



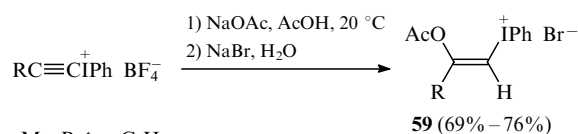
R = PhCH₂, PhCH₂CH₂, Bu^t, n-C₈H₁₇, cyclo-C₅H₉CH₂; X = Cl, Br.

The conjugate addition of sulfinic acids in methanol affords stereoselectively (*Z*)-(β-sulfonylvinyliodonium salts.^{94, 95}



$\text{R}^1 = \text{Me}, \text{Ph}(\text{CH}_2)_3, n\text{-C}_8\text{H}_{17}, \text{cyclo-C}_5\text{H}_9\text{CH}_2, \text{HO}(\text{CH}_2)_2, \text{cyclo-C}_6\text{H}_{11}(\text{CH}_2)_2; \text{R}^2 = \text{Ph}, 4\text{-NO}_2\text{C}_6\text{H}_4, 4\text{-MeOC}_6\text{H}_4, \text{Bu}^n.$

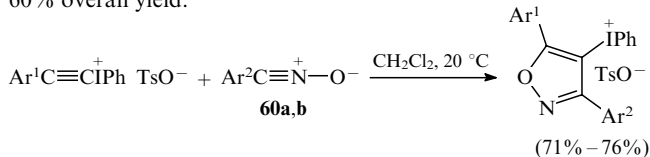
Recently, a similar approach was used to synthesise (*Z*)-(β -acetoxyvinyl)phenyliodonium bromides **59**.⁹⁶ The reaction sequence includes the conjugate addition of sodium acetate to alkynyliodonium salts in acetic acid and anion exchange in an aqueous solution of sodium bromide. The yields of the products **59** depend on the amount of sodium acetate added. The use of 0.1 equiv. of sodium acetate is optimum; the addition of a greater amount of sodium acetate decreases the yields of the targeted products considerably.⁹⁶



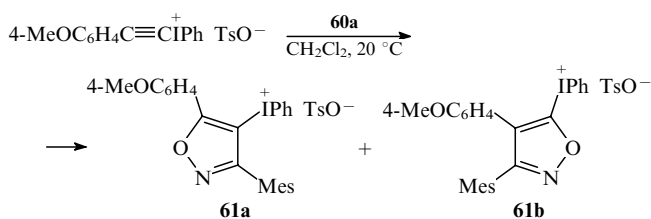
$\text{R} = \text{Me}, \text{Bu}^t, n\text{-C}_8\text{H}_{17}.$

Alkynyliodonium salts represent activated electron-deficient alkynes with a highly polarised triple bond. Owing to their dipolar structures, these compounds can be used as dipolarophiles in a variety of cycloaddition reactions. This provides a way to the synthesis of diverse alkenyliodonium salts.

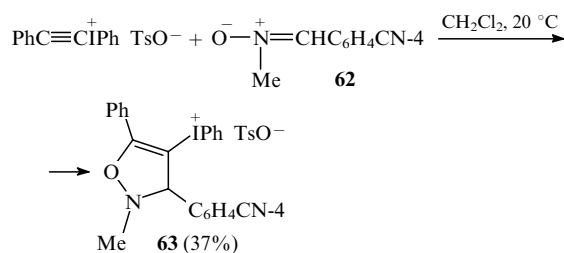
Thus (arylethynyl)iodonium tosylates react with nitrile oxides **60a,b** to form cycloadducts in high yields.⁹⁷ The reaction of [(4-methoxyphenyl)ethynyl]iodonium tosylate under similar conditions leads to a 1 : 1 mixture of two isomeric adducts **61a** and **61b** in 60% overall yield.⁹⁷



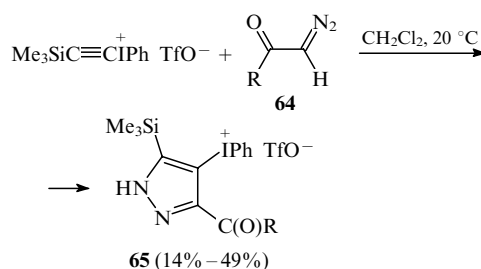
$\text{Ar}^1 = \text{Ph}, 2\text{-ClC}_6\text{H}_4; \text{Ar}^2 = \text{Mes} \text{ (a)}, 2,6\text{-Cl}_2\text{C}_6\text{H}_3 \text{ (b)}.$



Nitrone **62** reacts with (phenylethynyl)iodonium tosylate to give adduct **63**.⁹⁷

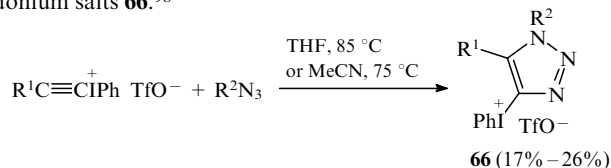


Diazocarbonyl compounds **64** form the corresponding cycloadducts **65** in the reactions with phenyl(2-trimethylsilyl)ethynyl)iodonium triflate.⁹⁸



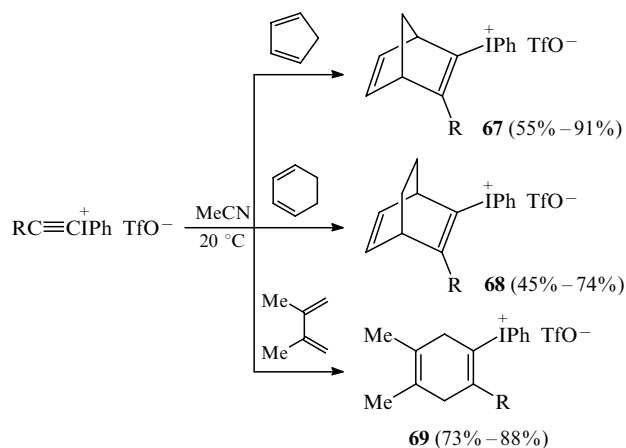
$\text{R} = \text{OMe}, \text{OEt}, \text{Ph}, \text{Bu}^t.$

Methyl and phenyl azides react with alkynyliodonium triflates on heating in tetrahydrofuran or acetonitrile to give triazolyl-iodonium salts **66**.⁹⁸



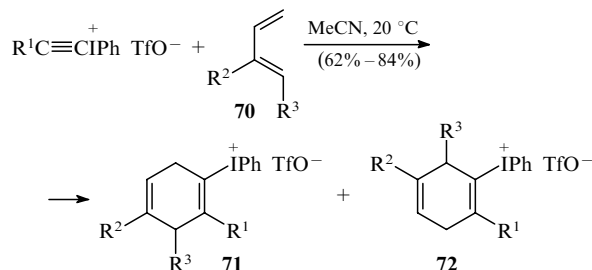
$\text{R}^1 = \text{H}, \text{Bu}^t; \text{R}^2 = \text{Me}, \text{Ph}.$

Alkynyliodonium salts can add not only to 1,3-dipolarophiles, but also to 1,3-dienes.⁹⁹ Adducts **67–69** are obtained as stable, crystalline compounds. Owing to the presence of two functional groups, these adducts can then be used in further reactions.

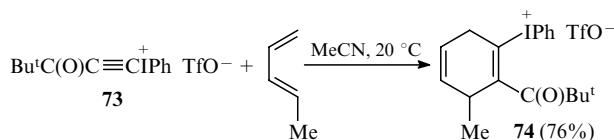


$\text{R} = \text{CN}, \text{Ts}, \text{PhCO}, \text{furan-C(O)}, \text{thiophene-C(O)}.$

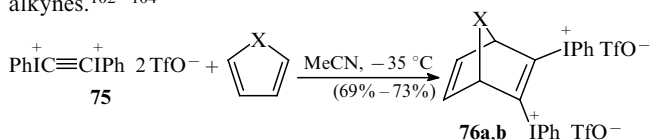
The reactions of alkynyliodonium salts with unsymmetrically substituted dienes **70** lead to mixtures of two regioisomeric cyclohexadienes **71** and **72** in 62%–84% overall yields.¹⁰⁰ Usually, the regioselectivity of the reactions with 2-substituted dienes is low, whereas 1-substituted dienes react more regioselectively. Thus the reaction of penta-1,3-diene with the alkynyliodonium salt **73** leads exclusively to the regioisomer **74**, the structure of which was unequivocally established by X-diffraction analysis.¹⁰⁰



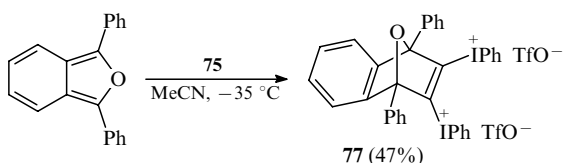
$\text{R}^1 = \text{CN}, \text{Ts}, \text{PhCO}, \text{furan-C(O)}, \text{thiophene-C(O)}, \text{Me}_2\text{NC(O)};$
 $\text{R}^2, \text{R}^3 = \text{H}, \text{Me}, \text{Et}, \text{Bu}^t.$



Acetylene bisiodonium salt **75** is more reactive and readily enters into reactions with cyclopentadiene, furan and 1,3-diphenylisobenzofuran in acetonitrile under mild conditions.¹⁰¹ The adducts **76a,b** and **77** are stable and can be used in further reactions with various nucleophiles or in cross-couplings with alkynes.^{102–104}



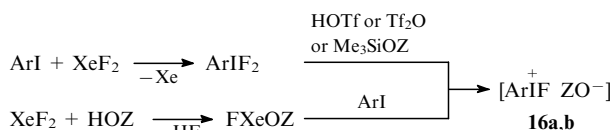
X = CH₂ (**a**), O (**b**).



7. Synthesis starting from fluoro(hydroxy)- λ^3 -iodanylarene sulfonates

Most of trivalent iodine organic derivatives employed in the synthesis of stable vinyliodonium salts are insufficiently reactive. Their electrophilicity can be enhanced if these compounds are converted into derivatives of strong acids containing highly nucleofugal groups as ligands. In this approach, reactive iodonium compounds are obtained in two steps, and the first step is the synthesis of readily available I(III)-derivatives from aryl iodides.

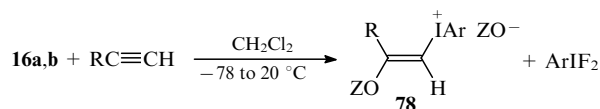
A new one-step procedure for the generation of iodonianylarenes directly from aryl iodides has been proposed recently.^{105–108} It was found that oxidation of aryl iodides with fluoroxenon sulfonate results in the formation of iodonium salts **16a,b**. The latter represent convenient starting compounds for the synthesis of diverse diaryl- and alkenyl-iodonium sulfonates. Compounds **16a,b** can also be obtained by the reactions of difluoriodanilyarenes with the respective sulfonic acid, its anhydride or trimethylsilyl ester.¹⁰⁵


$$Z = \text{Tf}(\mathbf{a}), \text{Ms}(\mathbf{b}).$$

The fact that the reagents **16a,b** contain the highly nucleofugal sulfonate group makes them important. These compounds probably have an ionic structure. It is worth noting that the reagents **16** represent only a specific example of compounds of the general formula $[\text{ArI}^+ \text{X Z}^-]$ where X and Z denote a heteroatomic substituent and a nucleofugal group, respectively. For example, derivatives with $\text{X} = \text{OH}$, $\text{Z} = \text{OTf}$;⁸² $\text{X} = \text{OH}$, $\text{Z} = \text{FSO}_3$;⁴¹ $\text{X} = \text{OH}$, $\text{Z} = \text{HSO}_4$;⁷ $\text{X} = \text{OH}$, $\text{Z} = \text{BF}_4$;⁴¹ $\text{X} = \text{F}$, $\text{Z} = \text{BF}_4$ (Refs 41, 62) are also known. In most instances, the structures of these compounds have not been strictly established. Several of them were deduced on the grounds of chemical transformations of these intermediates in reactions with various organic substrates. For example, the reactions with alkynes, aromatic compounds and enol silyl ethers gave rise to iodonium salts^{41, 58, 59, 62, 82} and β -diketones.⁴¹

Fluoro(hydroxy)iodanylarene sulfonates **16** react stereoselectively with terminal alkynes to form (*E*)-[β -(sulfonyloxy)alk-1-

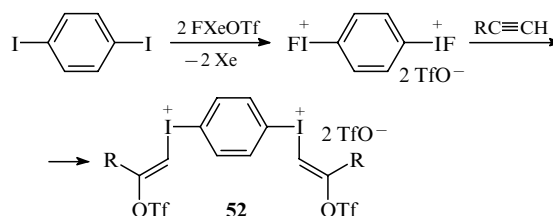
enyl](aryl)iodonium sulfonates **78**;^{105, 109} the structure of one of these compounds was proved by X-diffraction analysis.¹⁰⁸



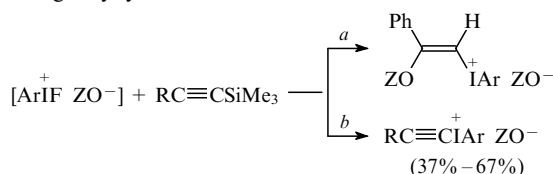
Z = Tf, Ms; Ar = Ph, 4-MeC₆H₄, 2-MeC₆H₄, 4-NO₂C₆H₄;

R = H, Prⁿ, Buⁿ, n-C₈H₁₇, CH₂OH, CH₂OMe, CH₂Cl, CH₂CH₂OH.

Earlier, (*E*)-(2-trifluoromethylsulfonyloxyvinyl)(aryl)iodonium sulfonates **78** were obtained by the electrophilic addition of the [PhIO–HOTf] reagent to alkynes.⁸² However, the synthesis of β -functionalised vinyliodonium salts by this method required an additional step including the conversion of iodobenzene into iodosobenzene followed by the activation of the latter with methanesulfonic acid. Compared with this procedure, the use of a novel oxidant, *viz.*, fluoroxenon sulfonate, which already contains the sulfonate group, allows a one-step preparation of β -functionalised vinyliodonium salts directly from iodobenzene and terminal alkynes. In addition, the reagents **16** are more reactive towards alkynes than the system [PhIO–HOTf], and readily enter into reactions even at $-70\text{ }^{\circ}\text{C}$. This method was shown to be suitable for the synthesis of bis(alkenyl)-*p*-phenyleneiodonium salts **52**.¹¹⁰


$$R = \text{H, Me, Et, Ph, Pr}^n, n\text{-C}_8\text{H}_{17}, \text{CH}_2\text{Cl}.$$

It is important to note that exclusively *Z*-alkenylidonium salts are formed in the reactions with phenyl(trimethylsilyl)acetylene.^{106, 109} The structure of one of such salts has definitively been established by means of X-diffraction analysis.¹⁰⁶ This stereochemical result differs in principle from other cases where adducts of iodosobenzene with fluorosulfonic or trifluoromethanesulfonic acid^{81, 82} reacted with alkynes to give *E*- β -substituted iodonium salts. It should also be noted that the reactions of other alkynyl-trimethylsilanes with the reagents **16a,b** give rise to the corresponding alkynylidonium salts.



Z = Tf: Ar = Ph (58%), *p*-MeC₆H₄ (53%); Z = Ms, Ar = Ph (56%);

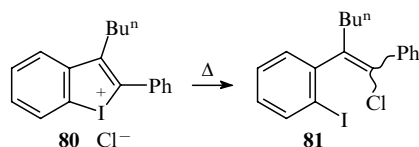
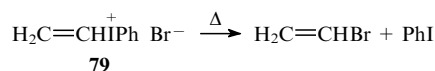
(a) R = Ph, HOZ, CH₂Cl₂, -78 to 20 °C;

(b) R = H, Buⁿ, Bu^t, MeOCH₂, CH₂Cl; CH₂Cl₂, -78 to 20 °C.

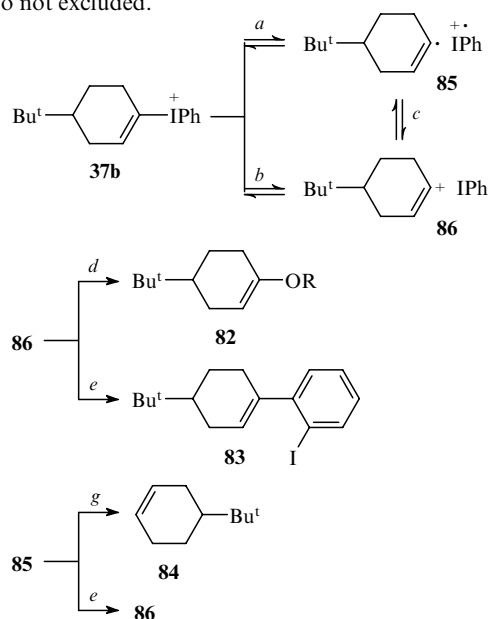
III. Reactions of alkenyliodonium salts

Exploration of chemical properties of alkenyliodonium salts was begun only in the mid-1980s. Although the majority of alkenyliodonium salts are rather stable compounds and can be stored for a relatively long time without any noticeable changes, most of them undergo thermal destruction on heating. As a rule, the thermal decomposition of alkenyliodonium salts involves the cleavage of a bond between I^+ and the carbon atom of the alkenyl fragment. Thermolysis of *trans*-chlorovinylidonium salts is accompanied by the formation of acetylene.^{42,43,46} Iodobenzene and vinyl bromide in the ratio of 1 : 1 are formed upon thermal decom-

position of solid phenyl(vinyl)iodonium bromide **79**; no other products have been detected.⁴⁶ Thermal decomposition of a cyclic iodonium salt **80**, which occurs at a melting temperature, leads to a mixture of substituted *cis*- and *trans*-stilbenes **81**.⁴⁹

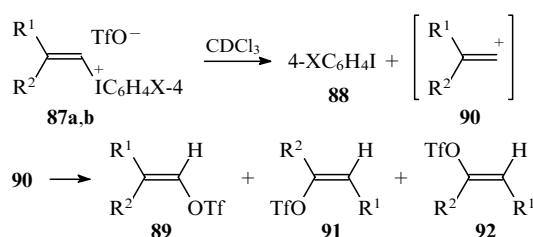


Alkenyliodonium salts undergo solvolysis and fragmentation. The mechanism of solvolysis of (4-*tert*-butylcyclohex-1-enyl)phenyliodonium tetrafluoroborate (**37b**) in ethanol and aqueous solutions was examined.¹¹¹ It was shown that the phenyliodonio group is about 10⁶ times as good a leaving group as the triflate. In addition to the expected products, *viz.*, **82** and iodobenzene, the solvolysis also yielded the internal return product **83** and a small amount of 4-*tert*-butylcyclohexene (**84**) resulting from a single-electron transfer. A mechanism involving initial heterolysis to form a contact ion pair **85** followed by a single-electron transfer to lead to an intermediate **86** was suggested. However, a possibility that the species **86** is formed upon homolysis of the C–I⁺ bond is also not excluded.



(a) C–I⁺ bond heterolysis; (b) C–I⁺ bond homolysis; (c) single-electron transfer; (d) ROH (solvolysis); (e) internal return; (g) –PhI.

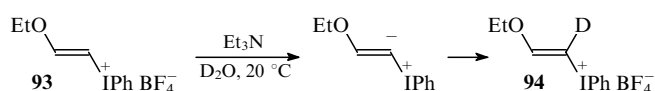
Fragmentations of 2,2-disubstituted alkenyliodonium salts **87a,b** in CDCl₃ follow a similar mechanism. However, in this case, triflates **91** and **92** are formed as the products of a cationic rearrangement of an intermediate **90** together with the solvolysis products **88** and **89**.¹¹²



R¹ = R² = Me, X = CF₃ (**87a**); R¹ = Ph, R² = Et, X = H (**87b**).

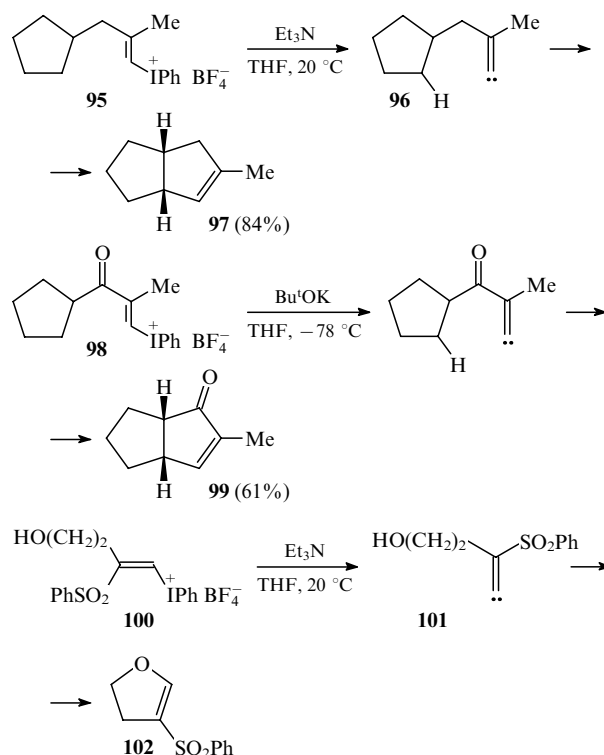
Obviously, the presence of the I⁺ArX[–] fragment significantly affects the electron density distribution not only in the groups vicinal to this fragment, but also in the molecule as a whole. Thus according to the ¹H NMR spectra of *E*- and *Z*-alkenyliodonium salts, the α-proton of the alkenyl group (with respect to the I⁺Ar fragment) is rather acidic.^{58, 61} The I⁺ArX[–] group is also responsible for the substantially enhanced C–H acidity of some other compounds.¹¹³

Being highly acidic, the α-hydrogen atom can readily be removed from alkenyliodonium salts even by such weak bases as amines.^{78, 114} An exchange of deuterium for the α-vinyl proton and to form deuterio-derivative **94** takes place upon treatment of (*E*)-(2-ethoxyvinyl)phenyliodonium salt **93** with triethylamine and D₂O in THF. The reaction presumably involves the intermediate formation of a vinylidene ylide **45**.¹¹⁴



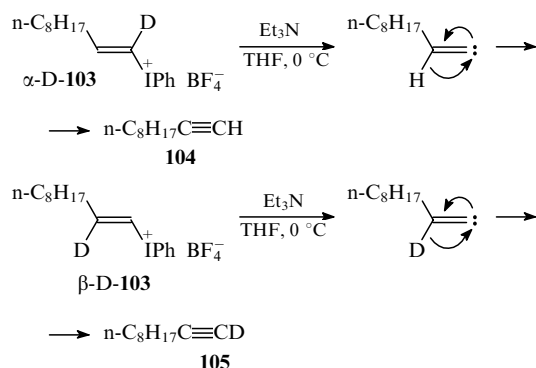
1. Generation of alkylidenecarbenes from vinylidene salts

Owing to the high nucleofugality of the I⁺ArX[–] group, vinylidene salts readily undergo reductive elimination of iodobenzene generating thereby highly reactive alkylidenecarbenes. The latter can further transform into cyclopentenones through an intramolecular regioselective insertion into the C–H bond (1,5-insertion). Thus α-elimination in the iodonium salt **95** followed by the 1,5-insertion in the species **96** proceed under mild conditions (Et₃N, 25 °C) yielding 2-methylbicyclo[3.3.0]oct-1-ene (**97**). Similarly, the ketone **99** is obtained from the iodonium salt **98**.¹¹⁵ This procedure can also be applied to alkenyliodonium salts bearing the OH group. Thus compound **100** eliminates iodobenzene to produce carbene **101**, which then inserts into the O–H bond to form 2,3-dihydrofuran derivative **102**.⁹⁵

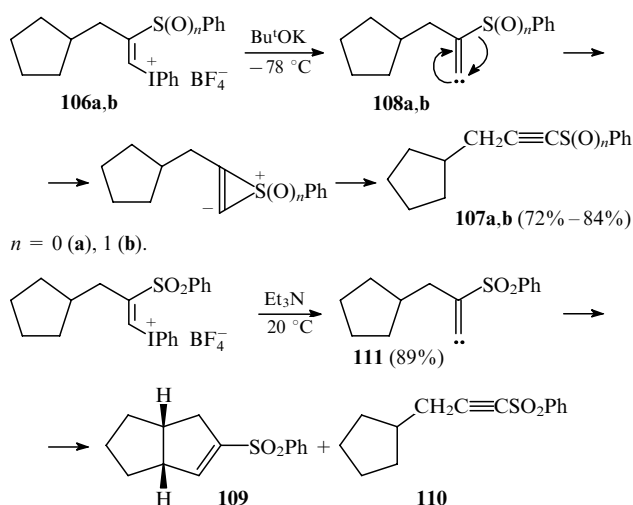


Reactions of deuterated alkenyliodonium salts **103** with triethylamine at 0 °C lead to terminal alkynes **104** (10% deuterium) and **105** (89% deuterium) in quantitative yields. The compositions of the reaction products indicate that alkylidenecarbenes predominantly arise through α-elimination and subsequent 1,2-hydrogen shift rather than through a *syn*-β-elimination process.¹¹⁵ The absence, in the reaction mixture, of cyclopentene

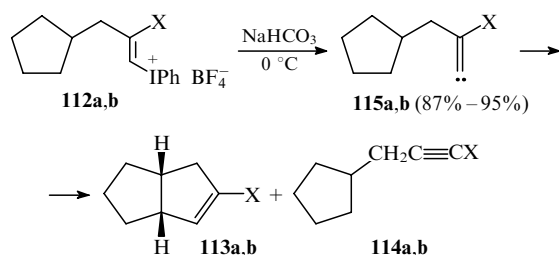
derivatives suggests that the 1,2- α -hydrogen shift following 1,5-insertion of alkylidenecarbenes into the C–H bond is very unfavourable.¹¹⁶



Elimination of iodobenzene from iodonium salts **106a,b** under the action of potassium *tert*-butoxide leads to alkynes **107a,b** as the main products. The α -phenylthio and α -phenylsulfonyl groups in alkylidenecarbenes **108a,b** are good leaving groups. Their migration apparently occurs *via* sulfonium ylides.⁹⁵ In contrast to compounds **106a,b**, an iodonium salt with the α -phenylsulfonyl group gives predominantly 2-phenylsulfonylbicyclo[3.3.0]oct-1-ene (**109**) (the ratio **109** : **110** = 4 : 1). This shows that the carbene **111** preferentially inserts into the C–H bond rather than undergoes migration of the sulfur-containing substituent despite the very good migrating ability of this group.¹¹⁶

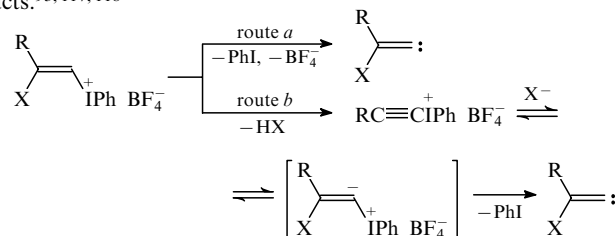


Reactions of halogen-containing alkenyliodonium salts of similar structures yield different products depending on the nature of the halogen atom in these salts. Thus chlorine-substituted salt **112a** gives a 38 : 62 mixture of the product of 1,5-insertion of a carbene into the C–H bond (**113a**) and the rearrangement product (**114a**). Only bromoalkyne **114b** is formed from the bromine-substituted salt **112b** due to the more preferable migration of the bromine atom in the carbene **115b**.⁹³

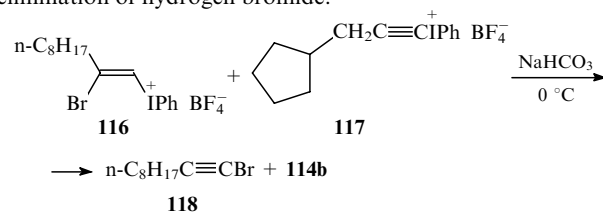


X = Cl (**a**), Br (**b**).

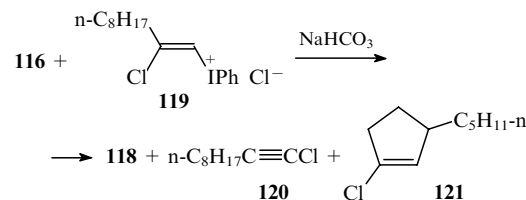
α -Halogenoalkylidenecarbenes are generated in the α -elimination of iodobenzene from (*Z*)-(2-halogenoalkenyl)iodonium salts (route *a*). However, in this case the reaction apparently also involves the more stereoelectronically favourable base-induced *anti*- β -elimination of HX giving rise to alkynyliodonium salts (route *b*). The Michael addition of a halide ion and subsequent reductive elimination of iodobenzene lead to the final products.^{93, 117, 118}



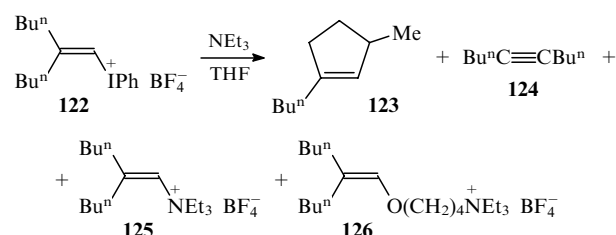
Possible transformations of the carbene formed were elucidated in a cross-reaction of (*Z*)-(2-bromoalkenyl)iodonium **116** and alkynyliodonium tetrafluoroborates **117** with sodium hydrogencarbonate. Alkynes **118** and **114b** were formed in the ratio 7 : 3, thus indicating that α -bromoalkylidenecarbene is generated through both α -elimination of the phenyliodonio group and *anti*- β -elimination of hydrogen bromide.⁹³

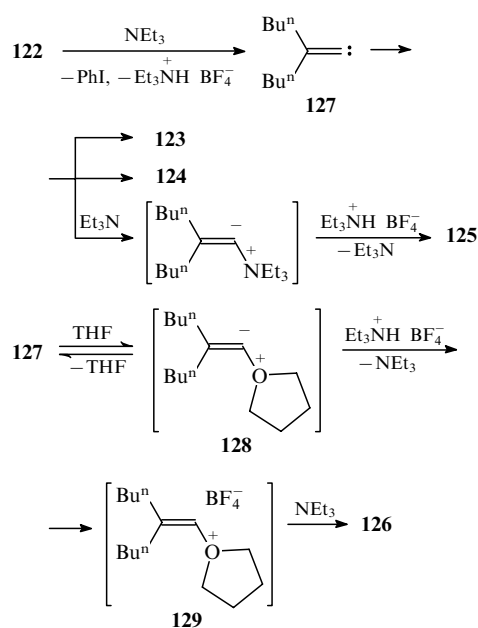


2-Bromovinylidonium salt **116** more readily undergoes *anti*- β -elimination than the 2-chlorovinylidonium salt **119**. This follows from the fact that a 78 : 13 : 9 mixture of compounds **118**, **120** and **121** is formed in the cross-reaction of both salts with NaHCO₃.⁹³



The direction of reactions involving the intermediacy of alkylidenecarbenes was found^{119–121} to be also dependent on the nature of solvent employed. In diethyl ether or THF, the complexation of alkylidenecarbenes with these solvents, *viz.*, the formation of oxonium ylides, was observed. Thus treatment of alkenyliodonium salt **122** with triethylamine in THF yields a mixture of products **123–125** formed as the result of 1,5-insertion of the carbene **127** into the C–H bond, 1,2-migration of the butyl group and also the reaction of salt **122** with triethylamine. In addition, a nucleophilic attack of the intermediate carbene **127** on tetrahydrofuran to form oxonium ylide **128** and further transformation of the latter into compound **126** *via* oxonium salt **129** also occur.¹²²





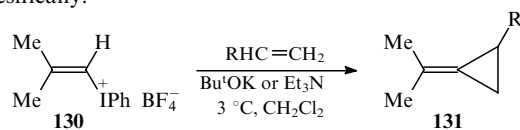
The course of the reactions is also controlled by the temperature (Table 1). On lowering the reaction temperature, the yields of the products **123**–**125** derived from alkylidenecarbene **127** are decreased, and the yield of the ether **126** derived from vinyl-oxonium ylide **128** is increased. These effects were explained as the reversibility of the process of oxonium ylide **128** formation, although no solid proof for the existence of an equilibrium between free alkylidenecarbenes and oxonium ylides was obtained.

Table 1. The ratio of the reaction products of compound **122** with Et₃N in THF.

Temperature /°C	Time /h	Overall yield (%)	Yields of reaction products (%)				Ratio (123 + 124 + 125) : 126
			123	124	125	126	
60	10	90	74	14	<1	2	98:2
40	10	95	75	11	<1	9	90:10
20	10	99	75	8	1	15	85:15
0	10	98	71	3	1	23	77:23
0 ^a	10	78	48	2	1	27	65:35
0 ^b	10	87	44	2	1	40	54:46
0 ^c	10	92	44	3	3	42	54:46

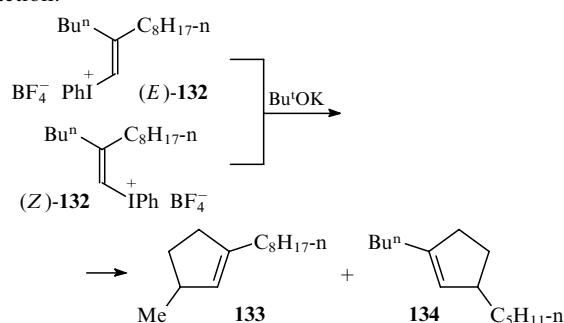
Note. The reaction mixture was preliminarily kept for 2 days at: ^a –20 °C; ^b –40 °C; ^c –60 °C.

An alkylidenecarbene generated from the alkenyliodonium salt **130** adds to alkenes to give alkylidenecyclopropanes **131**.¹²³ Its addition to *cis*- and *trans*-4-methylpent-2-enes occurs stereospecifically.

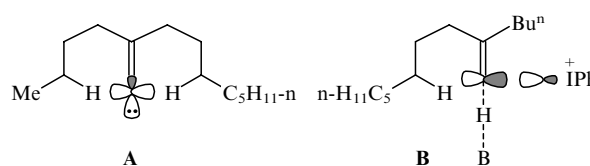


The ratio of isomeric cyclopentenes **133** and **134** formed upon treatment of both *Z*- and *E*-isomers of the iodonium salt **132** with Bu^tOK is 1:1 and is independent of the geometry of the starting compounds or the reaction conditions. This suggests the partic-

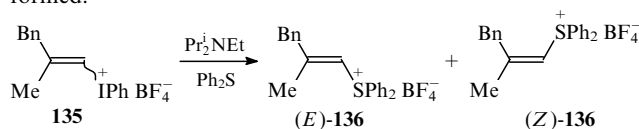
ipation of the alkylidenecarbene as an intermediate species in this reaction.¹¹⁵



Complete loss of regioselectivity testifies that this intermediate species represents a 'true' carbene (structure **A**) rather than a carbenoid (structure **B**) in which the 'memory effect' would be preserved to some extent.



In the presence of sulfides, alkylidenecarbenes give vinyl-sulfonium salts as the products of onium species transformations. An assumption that these reactions occur *via* free alkylidenecarbenes was put forward on the grounds of stereochemical studies.¹²² Thus (*E*)-vinylsulfonium salt (*E*)-**136** was the major product [the ratio (*E*)-**136** : (*Z*)-**136** is 69 : 31] in the reactions of both *E*- and *Z*-iodonium salts **135** with diisopropylamine in the presence of diphenyl sulfide. Such stereoselectivity most likely results from different bulkiness of two α-substituents in the alkylidenecarbenes formed.

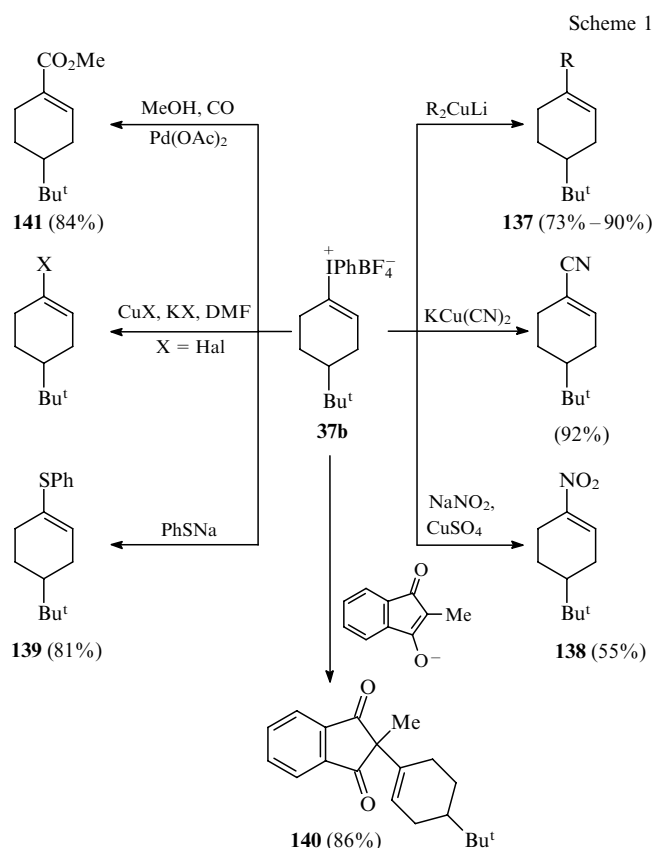


The ρ constants for the reactions of 2-methyl-1-propyliodene, generated from the salt **130**, with different styrene derivatives in the presence of Et₃N and Bu^tOK have been determined (–0.56 and –0.55, respectively) by measuring relative rates for these reaction.¹²³ Since free alkylidenecarbenes are relatively 'soft' nucleophiles, their reactions usually have small negative ρ values. In contrast, carbenoids generated from other precursors possess much more pronounced electrophilic properties and therefore their reactions have high negative ρ values.

2. Vinylic nucleophilic substitution in alkenyliodonium salts.

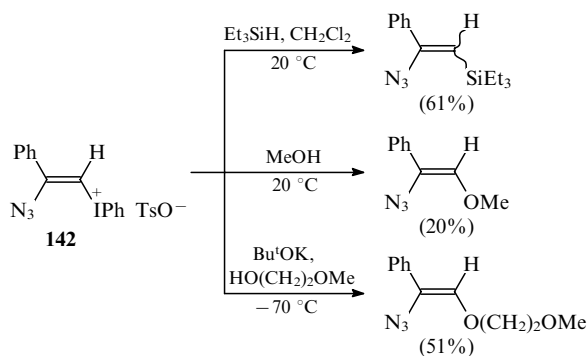
The arylidonio group is known to be one of the best leaving groups in nucleophilic substitution reactions.^{111, 124} Owing to the capability of aryl(vinyl)iodonium salts to generate vinylic cations under remarkably mild conditions, these salts can formally be considered as vinylic cation equivalents. The reactions of (4-*tert*-butylcyclohex-1-enyl)phenyliodonium tetrafluoroborate **37b** with various nucleophiles^{58, 59} are exemplified in Scheme 1.

Alkylation of alkenyliodonium salts with organometallic compounds to give substituted cyclohexenes **137** occurs successfully only with lithium organocuprates; other organometallic compounds are oxidised by the iodonium salt **37b**. Substitutions by halide ions in the presence of the respective copper(I) halides in DMF at 20 °C result in nearly quantitative yields of products. Good product yield is also obtained in the reaction with cyanide ion. The salt **37b** reacts with sodium nitrite in the presence of copper(II) sulfate to give nitroalkene **138** without any traces of

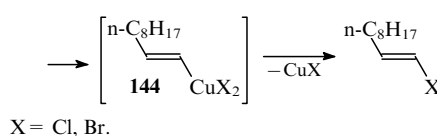
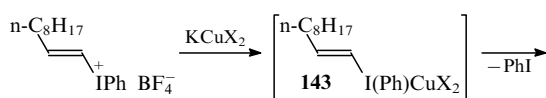


nitrite. The reaction with sodium benzenethiolate yields (4-*tert*-butylcyclohex-1-enyl) phenyl sulfide (**139**), while with indandione enolate it leads to the C-vinylation product **140** (see also Ref. 125). Vinyl iodonium salt **37b** is carbonylated in methanol in the presence of palladium salts as catalysts to afford ester **141**.

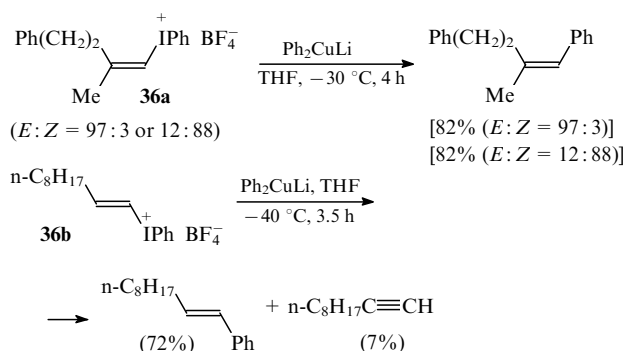
Reactions of several nucleophiles with 2-azidoalkenyl-iodonium salts **142** prepared *in situ* by the addition of sodium azide to alkynyliodonium salts have been studied.⁹⁰ In all cases, the iodine-containing fragment was substituted by nucleophiles.



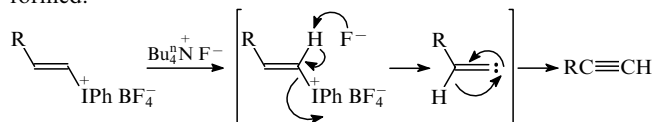
Nucleophilic substitutions of vinyl iodonium salts in the presence of copper compounds occur stereospecifically with retention of the initial configuration.^{126, 127} This was the reason to reject an idea of a free-radical mechanism for such reactions. Instead, a mechanism involving the intermediacy of three-coordinated iodine species **143** and three-coordinated copper **144** was suggested.^{102, 126, 127}



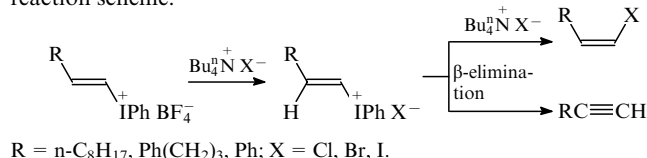
The stereochemistry of vinylic nucleophilic substitution has been studied in detail in the reactions of alkenyl(phenyl)iodonium salts **36a, b** with Ph_2CuLi in tetrahydrofuran. It was found that compound **36a** gives the products in high yields and with complete retention of the initial configuration. By contrast, the reactions of compound **36b** are accompanied by elimination to form the corresponding alkyne.⁵⁸



The substitution of the iodine-containing fragment in vinyl iodonium salts by halide, under the action of tetrabutylammonium halides in dichloromethane in the absence of copper(I) halides, occurs with inversion of configuration, which competes with elimination and the formation of alkynes.¹²⁸ Transformations of α - and β -deuterated substrates were examined in order to elucidate the mechanism of these reactions. Based on the results obtained¹²⁸ it was concluded that elimination in the reactions with $\text{Bu}_4\text{N}^+\text{F}^-$ results from the initial attack by the fluoride ion on the α -hydrogen atom followed by rearrangement of the carbene formed.



By contrast, other halide ions react through the β -elimination mechanism. The yields of elimination products are increased in the series: $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^-$; the dependence on the nature of a substituent at the C(2) atom has the order: *n*-alkyl < benzyl < phenyl. Stereoselectivity of the reactions decreases in the same order. With an increase in the excess of tetrabutylammonium halide in the reaction, a noticeable drop in the ratio alkyne : vinyl halide is observed, thus indirectly confirming the proposed reaction scheme.¹²⁸



Nucleophilic substitutions of the iodine-containing fragment in the iodonium salt **35** occur, as a rule, in good yields (Table 2); the ratio of stereoisomers depends on the nature of the nucleophile and the reaction conditions.⁵⁷

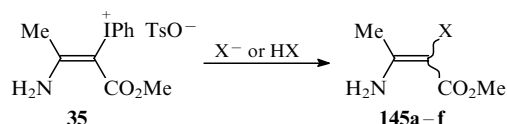
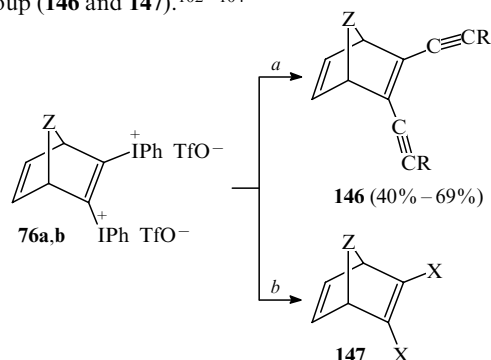


Table 2. Nucleophilic substitution of the iodine-containing fragment in compound **35**.

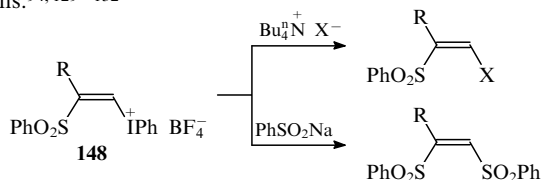
Product 145	X	Reaction conditions			Yield (%)
		reagent	solvent	time /h	
a	Br	Bu ₄ N ⁺ Br [−]	CH ₂ Cl ₂	12	78
b	NO ₂	NaNO ₂ , CuSO ₄	DMF, H ₂ O	12	20
c	TsO	TsONa	DMF	12	25
d	CN	KCN	DMF, H ₂ O	12	60
e	Et ₂ N	Et ₂ NH	CH ₂ Cl ₂	4	80
f			CH ₂ Cl ₂	4	83

Bisiodonium salts **76a,b** react with anionic nucleophiles to form the nucleophilic substitution products of the phenyliodonio group (**146** and **147**).^{102–104}



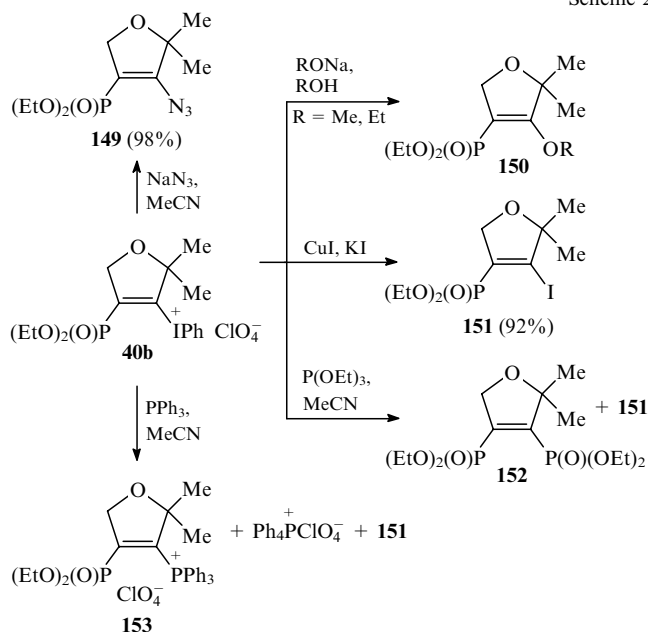
Z = O (**a**), CH₂ (**b**); (a) CH≡CR, BuLi, CuCN, CH₂Cl₂, −78 to 25 °C, 12 h, R = SiMe₃, Bu^t, Buⁿ, Ph; (b) NaX, CuX; X = Br, I, CN, PhCOO.

Nucleophilic substitutions in (Z)-(2-phenylsulfonyl)alkenyl-iodonium salts **148** with tetrabutylammonium halides or sodium benzenesulfonate proceed with retention of configurations.^{94, 129–132}



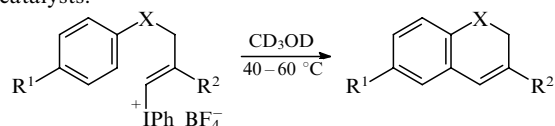
Heterocyclic iodonium salts also undergo nucleophilic substitution. Thus the reactions of compound **40b** with nucleophiles lead to the corresponding cyclic adducts through a two-step addition–elimination process and/or reductive elimination following attack by a nucleophile on the iodine atom (Scheme 2).⁶² Perchlorate **40b** reacts with sodium azide in acetonitrile to give vinyl azide **149** in nearly quantitative yield. The reactions of compound **40b** with sodium methoxide and sodium ethoxide in the respective alcohol afford vinyl ethers **150** in 83% and 91% yields, respectively. Compound **40b** reacts with a mixture of equimolar amounts of potassium and copper(I) iodides to give vinylic iodide **151** in 67% yield. In the reaction with triphenylphosphine, vinylic iodide **151** and the phenylation product of triphenylphosphine, *viz.*, tetraphenylphosphonium perchlorate (22% yield), are formed along with the expected vinylphosphonium salt **153** (20% yield).

Scheme 2

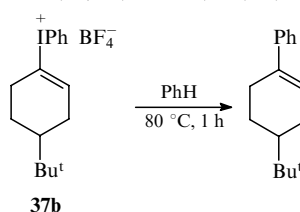


3. Vinylation of aromatic compounds with vinyliodonium salts

As is known, direct introduction of the vinylic group into aromatics by electrophilic substitution is rather inefficient because of the low reactivities of vinyl halides. Unlike vinyl halides, vinyliodonium salts do enter into the reactions of electrophilic aromatic substitution. These substitutions can proceed as an intramolecular process to lead to cyclic systems, if vinyliodonium salts have suitable structures.¹³³ Compared with Friedel–Crafts reactions they proceed under milder conditions and in the absence of catalysts.



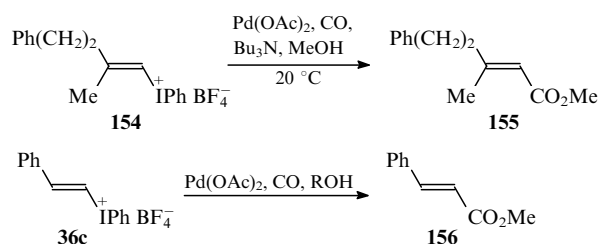
X = CH₂, O; R¹, R² = H, Me, Cl, Br.



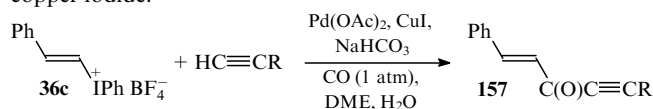
(Z)-Alkenyliodonium salts do not cyclise under the same conditions. An S_E(Ar)-substitution mechanism was suggested¹³³ in which iodobenzene is eliminated from the intermediate iodocyclopropane, though other mechanisms cannot be ruled out.

4. Palladium-catalysed cross-coupling

Vinyliodonium salts were found to undergo cross-couplings with activated alkenes. The reactions conditions are milder than those used in the Heck reaction. Thus salts **154** and **36c** are carbonylated in the presence of palladium at 20 °C with complete retention of configurations to form α,β-unsaturated esters **155** and **156**.^{58, 134}

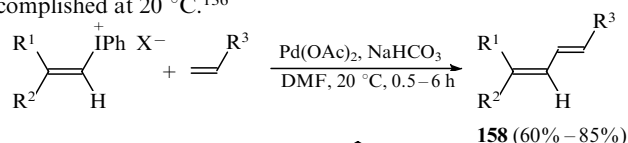


Enynones **157** were synthesised from alkenyliodonium salt **36c** and terminal alkynes under similar conditions in the presence of copper iodide.¹³⁵



R = Bu (76%), Ph (88%).

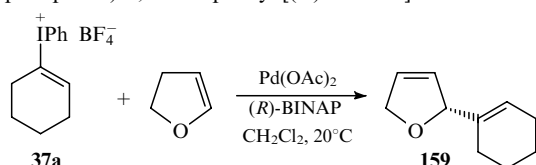
A highly stereoselective synthesis of conjugated dienes **158** is accomplished at 20 °C.¹³⁶



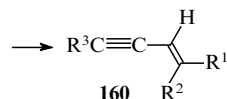
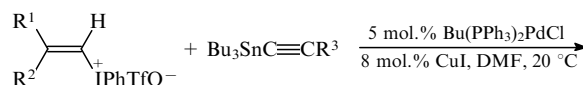
R¹ = H, Buⁿ, OTs; R² = Buⁿ, Ph, OTs,  ;

R³ = Ph, COMe, CO₂Me, CHO; X = OTs, BF₄.

An asymmetrical version of the Heck reaction was implemented in the presence of a chiral ligand, viz., (*R*)-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl [(*R*)-BINAP].¹³⁷

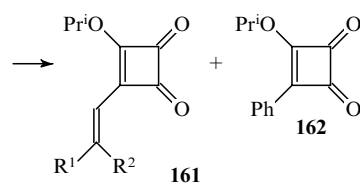
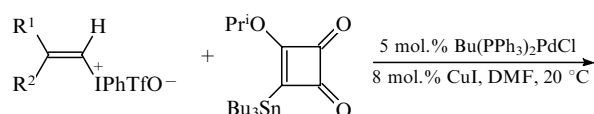


Furthermore, in the presence of palladium, alkenyliodonium salts react under mild conditions with alkynyl-,⁸⁶ allyl-¹³⁸ and alkenylstannanes.^{86, 138} The reactions with alkenylstannanes occur faster but less selectively to give various unidentified compounds along with the major product.



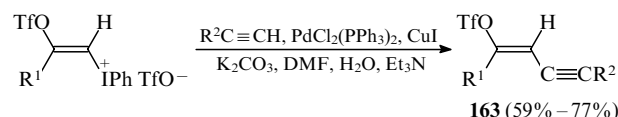
160

R ¹	R ²	R ³	Yield of 160 (%)
Bu ⁿ	Bu ⁿ	Ph	77
Me	Et	Ph	64
Et	Me	Ph	66
Bu ⁿ	Bu ⁿ	Bu ^t CO	66
Bu ⁿ	Et	C(O)N(CH ₂) ₄	67



R¹ = R² = Me (70%), R¹ = Buⁿ, R² = Et (60%);
R¹ = R² = Buⁿ (65%); R¹ = Et; R² = Buⁿ (76%).

Terminal alkynes readily react with alkenyl(aryl)iodonium salts bearing the TfO group in the β-position at 30–40 °C in DMF : H₂O (6 : 1) to form enynes **163** in high yields.¹³⁹



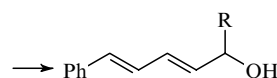
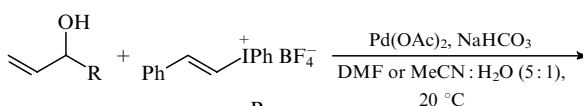
163 (59%–77%)

R¹ = Buⁿ, H, CH₂OMe, Ph; R² = n-C₈H₁₇, Ph, CH₂OMe, SiMe₃, CH₂Cl, Prⁿ.

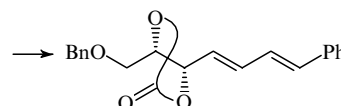
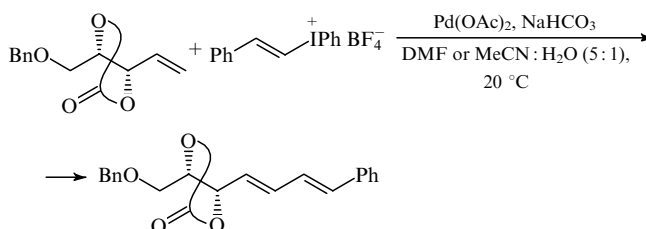
The reaction rates were found to be higher in polar solvents.¹³⁹ Small variations in the basicity of amines almost do not affect the reaction rates and the yields of the coupling products. Complexes of palladium with triphenylphosphine ligands were found to be the most efficient. The addition of CuI instead of CuI does not affect the reaction rates. An induction period (~1–2 h) is observed in the CuCl-catalysed reactions, after which the reaction rates become the same as in the case of CuI. The optimum ratio of PdCl₂(PPh₃)₂ to CuI is 2 : 3. The reaction rates are increased on addition of water to the system DMF–Et₃N–[Pd], this effect depending on the palladium catalyst employed. Thus the maximum rate acceleration on addition of water is observed in the presence of PdCl₂(PPh₃)₂.

In aqueous media in the presence of ligand-free palladium catalysts, unsubstituted alkenyliodonium salts also enter into reactions with terminal alkynes.¹⁴⁰

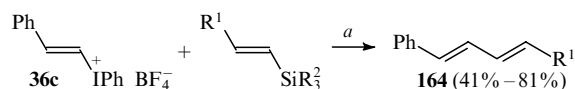
Alkenyliodonium salts react with allylic alcohols [in the presence of Pd(OAc)₂ (see Ref. 141) or a polymeric palladium catalyst¹⁴²] and allylic cyclic carbonates.¹⁴³



R = H, n-C₅H₁₁.



In the presence of palladium catalysts, alkenyliodonium salts also undergo the cross-coupling reactions with organoelement compounds.^{144–146} Thus, in the reaction of phenyl(styryl)-iodonium tetrafluoroborate **36c** with vinylfluorosilanes, only the β-styryl group was transformed to afford the cross-coupling products, dienes **164**, in high yields.¹⁴⁵

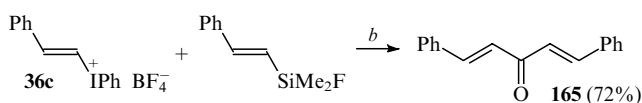


$\text{R}^1 = \text{Bu}^n, \text{Ph}; \text{R}_3 = \text{MeF}_2, \text{F}_3, \text{Me}_2\text{F};$

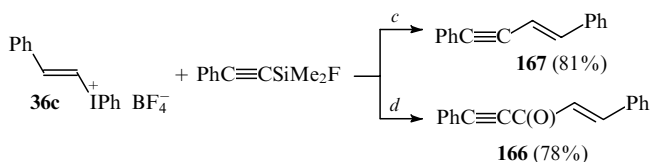
(a) $\eta^3\text{-C}_3\text{H}_5\text{PdCl}_2$, KF or $\text{Bu}_4\text{N}^+\text{F}^-$, DMF, 20 °C, 5 min.

To account for the palladium-catalysed reactions of vinylfluorosilanes with alkenyliodonium salts, a mechanism involving the interaction of an electrophilic alkenyliodonium salt with catalytically active Pd(0), the reductive elimination of iodobenzene to form alkenylpalladium tetrafluoroborate and the transmetallation reaction with vinylfluorosilanes was proposed.¹⁴⁵

Carbonylation of alkenyliodonium salts in the presence of Pd complexes^{145,146} can serve as a convenient procedure for the synthesis of unsaturated ketones, viz., **165** and **166**. Enyne **167** is smoothly obtained on coupling of alkynylfluoromethylsilane with the iodonium salt **36c**.¹⁴⁵



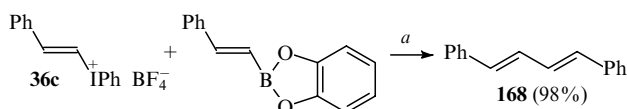
(b) $\eta^3\text{-C}_3\text{H}_5\text{PdCl}_2$, $\text{Bu}_4\text{N}^+\text{F}^-$, DME, CO (1 atm), 20 °C, 5 min.



(c) $\eta^3\text{-C}_3\text{H}_5\text{PdCl}_2$, KF or $\text{Bu}_4\text{N}^+\text{F}^-$, DMF, 20 °C, 5 min;

(d) $\eta^3\text{-C}_3\text{H}_5\text{PdCl}_2$, $\text{Bu}_4\text{N}^+\text{F}^-$, DME, CO (1 atm), 20 °C, 5 min.

The cross-coupling of alkenyliodonium salt **36c** with a large series of boronates in the system $\text{Pd}(\text{PPh}_3)_4\text{--Na}_2\text{CO}_3\text{--DMF--H}_2\text{O}$ has been effected and in all cases the cross-coupling product **168** was obtained in virtually quantitative yield.¹⁴⁴



(a) $[\text{Pd}(\text{PPh}_3)_4]$, Na_2CO_3 , DME : $\text{H}_2\text{O} = 4 : 1$, 20 °C, 10 min.

IV. Conclusion

From the data presented in this review one can see that alkenyliodonium salts are of interest for synthetic organic chemistry. These compounds are rather effective oxidants and can readily undergo free-radical transformations. They also possess high electrophilicities, which can be changed within a wide range by varying the ligands at the iodine atom, and are featured by the presence of the highly nucleofugal iodine-containing group.

Alkenyliodonium salts with several functional groups attract ever-growing interest. Such reagents allow the introduction into substrates of rather complex fragments under mild conditions.

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^a — *Russ. Chem. Bull. (Engl. Transl.)*

^b — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*

^c — *Russ. J. Org. Chem. (Engl. Transl.)*

^d — *Chem. Heterocycl. Compd. (Engl. Transl.)*

^e — *Russ. J. Gen. Chem. (Engl. Transl.)*

Metal complex catalysis in the synthesis of organoaluminium compounds

U M Dzhemilev, A G Ibragimov

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Abstract. The published data on the synthesis of organoaluminium compounds involving metal complex catalysts are generalised and systematised. Hydro-, carbo- and cycloalumination reactions of alkenes, conjugated dienes and alkynes catalysed by Ti and Zr complexes are considered in detail. The use of organoaluminium reagents in organic synthesis and novel reactions involving these compounds are discussed. The bibliography includes 240 references.

I. Introduction

About 40 years have passed since the discovery by Ziegler *et al.*¹ of a direct method for the synthesis of trialkylalanes based on the reaction of alkenes with activated aluminium and hydrogen. In this period, organoaluminium compounds (OAC) have become indispensable tools in practical synthetic and organometallic chemistry.

Fundamental studies into the chemistry of OAC carried out in the 1960's^{2–8} have formed the basis for the development of industrial methods for their synthesis. Special mention should be made of the investigations carried out by prominent Soviet specialists Zakharkin,^{9,10} Zhigach^{11,12} and Korneev^{13,14} who have developed and industrialised a wide range of practically important OAC including co-catalysts for polymerisation and oligomerisation of alkenes and dienes.¹⁵

The manufacture of OAC has considerably stimulated the interest of investigators in these compounds as promising reagents for fine organic and organometallic synthesis. The most important fields of their application include thermal hydroalumination of alkenes, dienes and alkynes; reduction of carbonyl compounds, esters and nitriles; synthesis of higher OAC and selective functionalisation of unsaturated compounds. The results of these studies are summarised in numerous reviews and monographs (see, *e.g.*, Refs 16–20).

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Studies by Tolstikov *et al.* (see Refs 18 and 19) deserve special mention, since they generalise the data on OAC as efficient reagents for organic synthesis. Thus the recently published monograph by Kouchin and Tolstikov¹⁹ provides a systematic description of the published data concerning the synthesis and conversions of OAC since 1970; however, more recent studies carried out in the last decade have not been cited in this book. Meanwhile, the fact that modern studies into the chemistry of OAC widely employ metal complex catalysis has made it possible not only to alter the strategy of organoaluminium synthesis but also to develop chemo-, regio- and stereoselective synthetic procedures for obtaining novel classes of OAC under mild conditions; these methods compete favourably with traditional approaches which utilise elevated pressures and temperatures.

The most efficient and widely employed catalysts for the reactions with OAC include Ti and Zr complexes and, in a lesser degree, Hf-, Co-, Ni-, V- and rare-earth element-containing compounds.

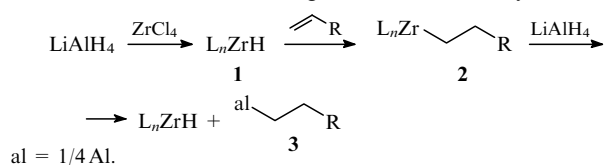
About ten years have passed since the publication of the reviews^{16,17} dealing with the application of metal complex catalysts based on Ti and Zr complexes in the synthesis and transformations of OAC. Numerous publications appeared in this decade and they were devoted to non-traditional catalytic methods for the synthesis of OAC. The present review summarises the most important published data on the application of metal complex catalysts in the synthesis of OAC by catalytic hydro-, carbo- and cyclo-metallation of alkenes, dienes and alkynes using the simplest alkylaluminium compounds and aluminium hydrides and systematises the data on the synthetic conversions of OAC in the presence of transition metal complexes.

II. Catalytic hydroalumination of alkenes

Thermal hydroalumination of mono-, di- and trisubstituted alkenes with OAC containing an Al–H bond is still one of the most popular methods for the synthesis of higher OAC.^{18–20} Unfortunately, this method suffers from a number of disadvantages which considerably restrict its application, *viz.*, hydroalumination has to be carried out at elevated temperatures (70–150 °C); moreover, this reaction is not suitable for all types of alkenes, since the presence of functional groups strongly complicates the results of reactions.

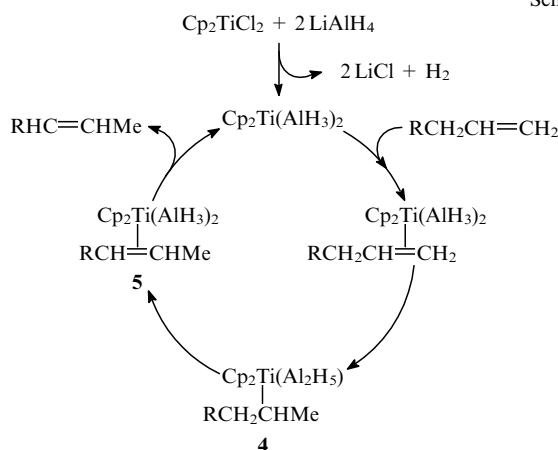
The reaction of LiAlH₄ with α -alkenes in the presence of Ti and Zr complexes is one of the first examples of catalytic hydro-

alumination under mild conditions (0–20 °C).²¹ This novel procedure allows the synthesis of lithium tetraalkylalanates in 60% to 100% yields. Sato *et al.*²¹ who studied the mechanism of catalytic hydroalumination of alkenes with LiAlH_4 in the presence of Zr complexes suggested that this reaction generates active hydride zirconium complexes **1**, which hydrozirconate alkenes with the formation of alkylzirconium complexes **2**. Transalkylation of the latter with LiAlH_4 gives lithium tetraalkylalanates **3**.



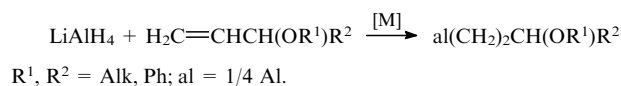
Using hydroalumination of hex-1-ene with lithium aluminium hydride as an example, it was shown²² that TiCl_4 , VCl_4 , Cp_2TiCl_2 and Cp_2ZrCl_2 manifest high catalytic activity comparable with that of ZrCl_4 . In the case of VCl_4 and Cp_2TiCl_2 , hydroalumination products were formed together with hex-2-ene resulting from isomerisation of the original hex-1-ene. The isomerisation of terminal alkenes in the presence of Cp_2TiCl_2 is shown in Scheme 1. The coordination of the central atom of the catalyst with an alkene results in the corresponding alkyltitanium σ -complex **4** in which the transfer of the hydride ion is accompanied by the formation of a complex **5** in the presence of an excess of the α -alkene. Decomposition of the complex **5** yields a mixture of stereoisomeric hex-2-enes.²³

Scheme 1



In their reactivities in the hydroalumination reaction, aluminium hydrides and alkenes can be arranged in the following orders:²⁴ $\text{LiAlH}_4 > \text{AlH}_3 > \text{AlH}_2\text{Cl} > \text{AlHCl}_2$; $\text{RCH}=\text{CH}_2 > \text{R}_2\text{C}=\text{CH}_2 > \text{RCH}=\text{CHR}$.

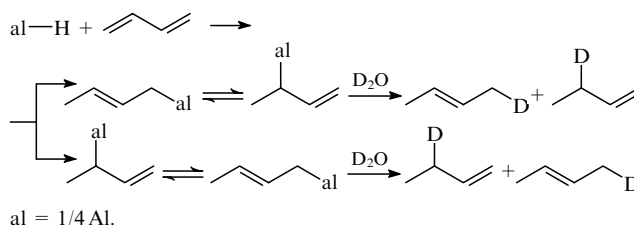
Co, Ni and Fe chlorides,^{25,26} Cr²⁷ and U²⁸ salts and transition metal complexes immobilised on inorganic²⁹ or polymeric supports^{29,30} can be used as catalysts in hydroalumination reactions. In contrast with thermal hydroalumination, catalytic hydroalumination in the presence of Zr and Ti complexes can also be performed in the presence of such functionally substituted alkenes as allylic alcohols and ethers.^{31–33}



Subsequent one-pot conversions of lithium tetraalkylalanates are of considerable practical interest. Thus cross-coupling of lithium tetraalkylalanates formed *in situ* with allyl halides in the presence of copper salts [CuBr , CuI , CuCN , CuCl_2 , $\text{Cu}(\text{OAc})_2$] yields alkenes which are three carbon atoms longer than the starting compounds;³⁴ the CuCl -catalysed reaction with propargyl bromide yields terminal allenes in high yields.³⁵ This reaction is one of the simplest and most convenient procedures for one-step conversion of alkenes into the corresponding allenes.

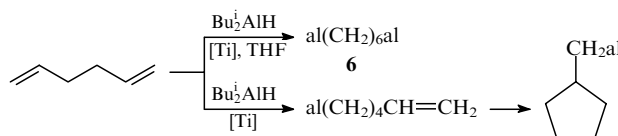
Later, cross-coupling was successfully extended to allenyl bromide,³⁶ carboxylic acid halides,³⁷ acrolein³⁸ and methyl vinyl ketone.^{38,39} Catalytic hydroalumination with LiAlH_4 and subsequent functionalisation of the alkylalanates formed makes it possible to convert the starting alkenes into the corresponding organic halides,⁴⁰ acetates⁴¹ or organoboron compounds⁴² in one step.

Unlike reactions with terminal alkenes, hydroalumination of 1,3-dienes with LiAlH_4 or NaAlH_4 in the presence of catalysts, such as Cp_2TiCl_2 or TiCl_4 occurs less selectively and affords 1,2-, 1,4- and 3,4-addition products.^{43,44}



Along with complex aluminium hydrides, readily available alkylaluminium hydrides are also used for catalytic hydroalumination of alkenes. In the example of hydroalumination of a mixture of isomeric decenes with Bu_2AlH in the presence of catalytic amounts of $\text{Ti}(\text{O}i\text{Bu})_4$, it was established that the terminal double bond enters into the reaction 154 times faster than the *cis*-disubstituted bond and 241 times faster than the *trans*-disubstituted bond.⁴⁵

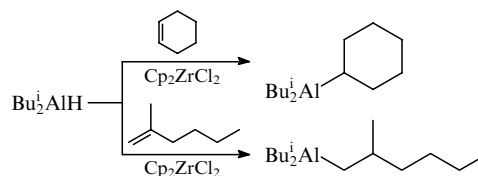
Hydroalumination of hexa-1,5-dienes with Bu_2AlH has a number of specific features. In the presence of $\text{Ti}(\text{O}i\text{Bu})_4$ as a catalyst (1.5 mol.%)⁴⁶ and without it⁵ hydroalumination occurs, which is followed by intramolecular cyclisation. However, when the reaction is carried out in solvents containing electron-donor atoms (N, O, S, P), no cyclisation takes place and the α,ω -dialuminium compound **6** is formed instead.⁴⁶ These data suggest that in the course of hydroalumination the starting hydrometallating reagent readily forms donor-acceptor complexes with the solvent owing to the lone electron pair of the heteroatom, which prevents the intramolecular cyclisation.



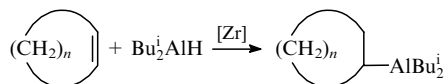
$[\text{Ti}] = \text{Ti}(\text{O}i\text{Bu})_4$, $\text{al} = 1/3 \text{ Al}$.

Commercially available diisobutylaluminium hydride can be used as an efficient hydroaluminating reagent for linear and cyclic mono-, di- and trienes including those containing functional groups. Zirconium complexes proved to be the most active catalysts in these reactions.^{16,47} Thus Bu_2AlH hydroaluminate α -, α,β -disubstituted and cyclic alkenes in high yields in the presence of ZrCl_4 even at $\sim 20^\circ\text{C}$ (3–6 h).⁴⁸ The use of titanium-containing catalysts results in the formation of side products as a result of isomerisation of the original alkenes.²³ This reaction virtually does not occur in the absence of the catalysts.

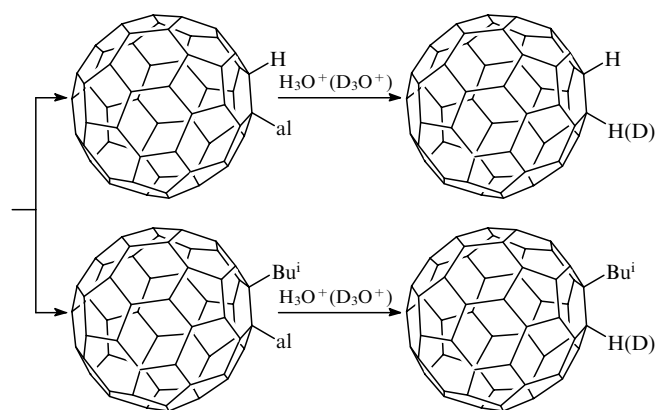
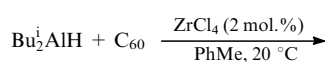
An analysis of the literature data on hydrozirconation of alkenes⁴⁹ prompts a conclusion that hydroalumination yields reactive zirconium hydride intermediates able to hydrozirconate alkenes; further transmetalation of alkyl and cycloalkyl zirconium complexes results in higher OAC.⁴⁸



Studies by Tolstikov *et al.*⁵⁰ have shown that zirconium chloroalkoxides $(\text{RO})_n\text{ZrCl}_{4-n}$ are more reactive catalysts of the hydroalumination reaction than ZrCl_4 or $\text{Zr}(\text{O}i\text{Bu})_4$. Therefore, a mixture of ZrCl_4 with Bu^iOH , MeOH , EtOH and Pr^nOH is used to obtain a reactive catalyst. The rate of cycloalkene hydroalumination depends on the ring size and decreases in the following order: $\text{C}_5 > \text{C}_6 > \text{C}_7 > \text{C}_{12} > \text{C}_8$.

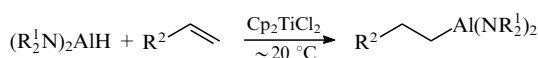


Hydroalumination of the C_{60} fullerene with Bu_2^iAlH in the presence of ZrCl_4 or $(\text{RO})_n\text{ZrCl}_{4-n}$ at $\sim 20^\circ\text{C}$ $\{\text{C}_{60}:[\text{Al}] = 1:(100-300), 24 \text{ h, toluene}\}$ was carried out by Ibragimov *et al.*^{51,52} Data from hydrolysis and deuteriolysis of fullerene-containing OAC suggest that these reaction conditions favour the formation of both hydro- and carboalumination products (total yield $\sim 90\%$).

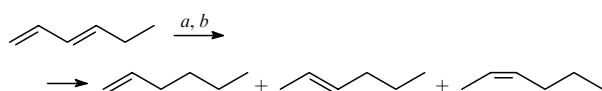


al = $1/3 \text{ Al}$.

Bis(dialkylamino)alanes manifest high reactivity in hydroalumination of alkenes, however, only in the presence of Cp_2TiCl_2 .^{53,54} These compounds hydroaluminate α -alkenes, methyldienealkanes and aliphatic disubstituted alkenes in practically quantitative yields. Cycloalkenes are less reactive in this reaction. Tri- and tetrasubstituted alkenes cannot be involved in this reaction.

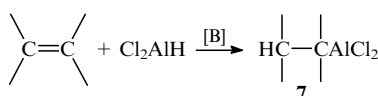


The advantage of bis(dialkylamino)alanes over dialkylalanes is in the feasibility to use them for catalytic hydroalumination of conjugated dienes; however, the selectivity of these reactions is rather low as in the case of complex hydrides.^{55,56}



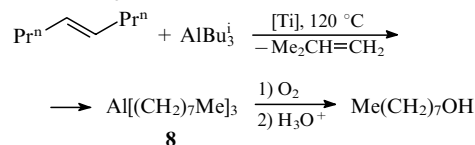
(a) $(\text{Pr}^i\text{N})_2\text{AlH}$, Cp_2TiCl_2 , THF, 12 h, 20°C ; (b) H_2O (55%).

Dichloroalane which reacts with alkenes in the presence of boron derivatives to give the corresponding higher alkyl-dichloroaluminium compounds **7**, is used as a reactive hydroaluminating reagent.⁵⁷⁻⁶⁰

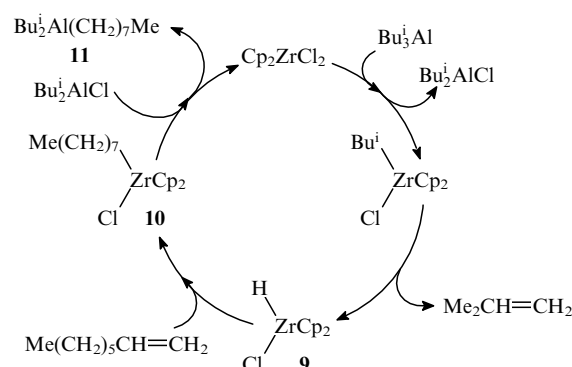


$[\text{B}] = \text{PhB}(\text{OH})_2$, $\text{B}(\text{OH})_3$, Et_3B , $\text{B}(\text{OMe})_3$, 9-borabicyclo[3.3.1]nonane (9-BBN), BF_3OEt_2 .

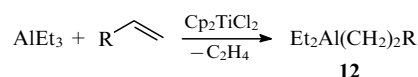
Hydroalumination of disubstituted alkenes with Bu_3^iAl in the presence of Ti^{4+} or Zr^{4+} salts at $110-120^\circ\text{C}$ gives predominantly OAC **8**.⁶¹ Apparently, the catalyst induces the isomerisation of the disubstituted double bond in the original alkenes into the terminal bond which is much more readily hydroaluminated with Bu_3^iAl .



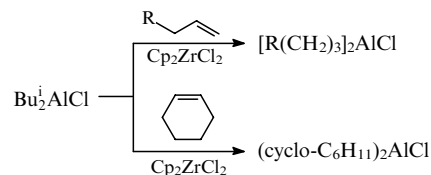
The yield of reaction products in hydroalumination of alkenes with Bu_3^iAl strongly depends on the nature of the catalyst. Thus in the presence of catalytic amounts of Cp_2ZrCl_2 , higher trialkylalanes can be synthesised from terminal alkenes and AlBu_3^i in high yields (0°C , 6 h).⁶² This reaction does not take place in the absence of the catalyst. Such a high reactivity of Bu_3^iAl in the presence of Cp_2ZrCl_2 can be attributed to the formation of zirconium hydrides **9**,^{63,64} which hydrometallate alkenes at low temperatures to give the complex **10**. Subsequent transmetalation of alkylzirconium complexes results in alkylalanes **11**.



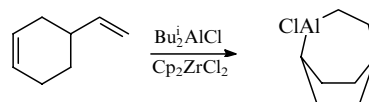
Hydroalumination of terminal alkenes with yet another hydroaluminating reagent, *viz.*, AlEt_3 in the presence of Cp_2TiCl_2 , follows a similar path and yields alkyl(diethyl)alanes **12**.⁶⁵

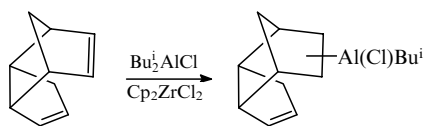


Higher dialkylaluminium chlorides cannot be synthesised by thermal transalkylation with Bu_2^iAlCl ; therefore, the use of Bu_2^iAlCl for Cp_2ZrCl_2 -catalysed hydroalumination of alkenes⁶⁶ which gives nearly quantitative yields should be regarded as a significant breakthrough.

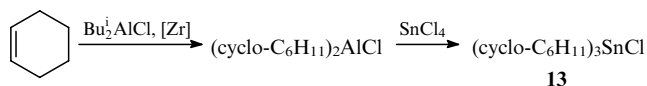


This reaction involves non-conjugated di- and trialkenes (including cyclic and functionally substituted ones).⁶⁷ Hydroalumination of norbornenes with Bu_2^iAlCl is stereoselective and affords the corresponding cycloalkylhalogenoalanes.⁶⁸ The reactions involving 4-vinylcyclohexene and dicyclopentadiene result in bi- and tri-cyclic halogenoalanes.

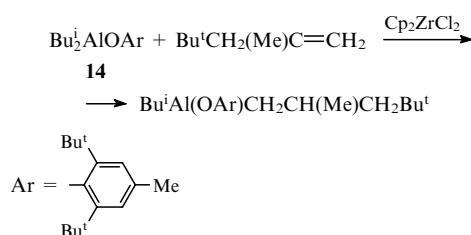




The Cp_2ZrCl_2 -catalysed hydroalumination of cyclohexene with Bu_2^iAlCl was successfully employed to obtain tricyclohexyltin chloride (**13**).⁶⁹

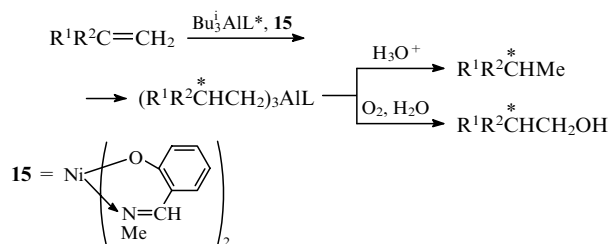


(2,6-Di-*tert*-butyl-4-methylphenoxy)diisobutylaluminium (**14**) was recommended for use as a regio- and stereoselective reagent for hydroalumination of alkenes and carbonyl compounds in the presence of a two-component catalyst, Cp_2ZrCl_2 –aluminium hydride (1:1).⁷⁰



Because of the low reactivity of reagent **14**, hydroalumination should be performed at high temperature (145 °C); however, the presence of a bulky aryloxy substituent ensures high regioselectivity of this reaction.

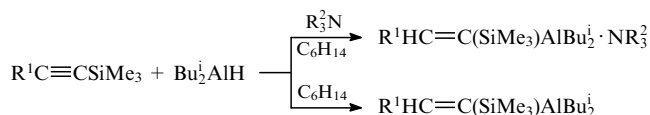
It was shown^{71, 72} that the exchange reaction between optically active solvates ($\text{L}^* \cdot \text{Bu}_3^i\text{Al}$) and disubstituted terminal alkenes in the presence of a nickel(II)–*N*-methylsalicylideneamine complex **15** gives optically active trialkylalanes; their further oxidation or hydrolysis results in optically active alcohols or hydrocarbons. (–)-*N,N*-Dimethylmenthylamine, (+)-(*S,S*)-2,3-dimethoxy-1,4-bis(*N,N*-dimethylamino)butane, (+)-*N,N*-dimethylbornylamine, (+)-(*R*)-*N,N*-dimethyl-1-phenylethylamine, *etc.* were used as chiral ligands which form solvates with AlBu_3^i .^{71, 72}



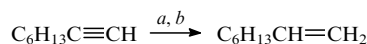
Hydroalumination of oxabicycloalkenes with Bu_2^iAlH can be carried out in the presence of $\text{Ni}(\text{COD})_2$ (COD is cyclooctadiene) or its derivatives with phosphines;⁷³ the regio- and enantioselectivity of this reaction largely depend on the ligand environment of the central atom of the catalyst.

III. Catalytic hydroalumination of alkynes

Non-catalysed hydroalumination of disubstituted acetylenes can be achieved by using Bu_2^iAlH , Et_2AlH or Bu_3^iAl under sufficiently mild conditions but is characterised by low selectivity, since the vinylalanes formed in this reaction undergo further transformations.²⁰ Hydrolysis of vinylalanes results in 1,2-disubstituted alkenes with a *Z*- or an *E*-configuration depending on the nature of the starting hydroaluminating reagent,⁷⁴ the structure of the alkyne⁷⁵ and the solvent.⁷⁶

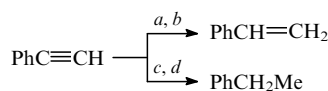


In the presence of transition metal complexes, hydroalumination of alkynes sometimes occurs with higher selectivity and in higher yields. For example, the reaction of oct-1-yne with Bu_2^iAlH in the presence of stoichiometric amounts of methylcuprate (1.25 h, 20 °C) and subsequent hydrolysis of the reaction mixture give oct-1-ene in a quantitative yield.⁷⁷



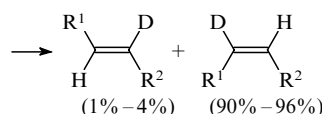
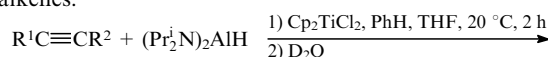
(a) Bu_2^iAlH , MeMgBr , CuCl , LiCl , THF; (b) H_2O (100%).

Hydroalumination of monosubstituted acetylenes normally yields a mixture of alkenes and alkanes, since mono- and dihydroalumination of the triple bond occur simultaneously. Selective mono- or dihydroalumination of alkynes can be carried out in the presence of Fe or Ni salts.²⁶



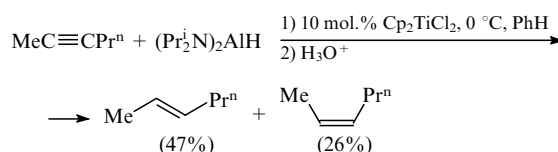
(a) LiAlH_4 , FeCl_2 , ~20 °C, 24 h; (b) H_2O (94%); (c) LiAlH_4 , NiCl_2 , ~20 °C, 24 h; (d) H_2O (99%).

Hydroalumination of mono- and disubstituted acetylenes with LiAlH_4 in the presence of TiCl_4 or Cp_2TiCl_2 can be carried out with high selectivity. Thus the reaction of oct-4-yne or hex-2-yne with hydride aluminium complexes [LiAlH_4 , NaAlH_4 , LiAlMe_3H , NaAlMe_3H , $\text{NaAl}(\text{OCH}_2\text{CH}_2\text{OMe})_2\text{H}_2$] in the presence of catalytic amounts of Cp_2TiCl_2 in THF yields alkenylalanes after 2 h at 20 °C; hydrolysis of the latter results in *cis*-oct-4-ene and *cis*-hex-2-ene, respectively (yields ~100%).⁷⁸ Aminoalanes can also be used for hydroalumination of alkynes.⁵³ In this case, hydroalumination of disubstituted acetylenes occurs with high selectivity and under milder conditions than that of terminal alkynes. Thus in the presence of 5 mol. % of Cp_2TiCl_2 , the reaction of methylphenylacetylene with $(\text{PrN})_2\text{AlH}$ gives alkenylalanes in a total yield of >95%.⁵⁴ The reaction of aminoalanes with disubstituted acetylenes predominantly occurs as the *cis*-addition, which makes it possible to use this method for the synthesis of *Z*-alkenes.



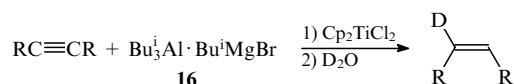
$\text{R}^1 = \text{Me}$; $\text{R}^2 = \text{Bu}^n$, $n\text{-C}_6\text{H}_{13}$, Ph ; $\text{R}^1 = \text{R}^2 = \text{Ph}$.

The composition of the reaction mixture depends on temperature, solvent and reaction time. Thus hydroalumination of hex-2-yne with $(\text{PrN})_2\text{AlH}$ in benzene at 0 °C yields a mixture of alkenylalanes with *trans*- and *cis*-configurations of the substituents. Their hydrolysis yields a mixture of isomeric hex-2-enes.⁵⁴

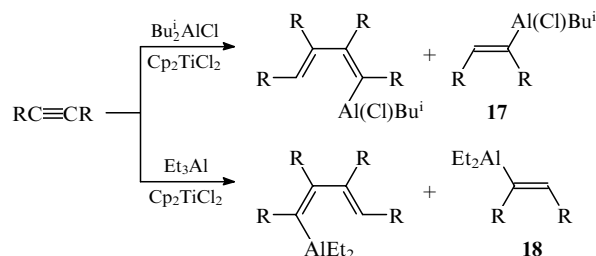


The aluminium-magnesium reagent **16** ($\text{Bu}_3^i\text{Al} - \text{Bu}^i\text{MgBr}$)⁷⁹ the efficiency of which is comparable with that of 9-BBN was

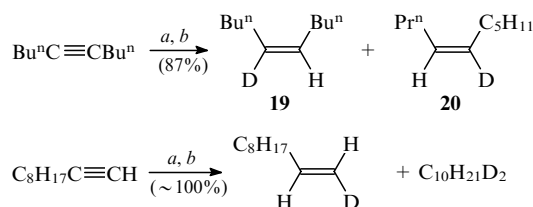
recommended for stereoselective hydrometallation of disubstituted acetylenes. This method is especially efficient in the conversions of disubstituted acetylenes into *Z*-alkenes. In the presence of 2 mol.% Cp_2TiCl_2 , the reaction with an excess of this reagent (3–10 equiv.) occurs at 20 °C and is completed within 20 min. *Z*-Alkenes are formed in 95%–98% yields and with ~98%–100% selectivity.



The recently synthesised reagents $\text{Bu}_2^i\text{AlCl}-\text{Cp}_2\text{TiCl}_2$ and $\text{Et}_3\text{Al}-\text{Cp}_2\text{TiCl}_2$, designed for selective hydroalumination of disubstituted acetylenes into the corresponding unsaturated OAC **17** and **18** the stereoselectivity of which is close to 100%, deserve special attention.^{80–82} Hydrolysis of OAC **17** and **18** results in *Z*-alkenes. Depending on the structure of the original alkynes and reaction conditions, 5% to 30% of alkadienylalanes are formed together with alkenylalanes. The structure of the unsaturated OAC **17** and **18** has been established by spectral methods.⁸³

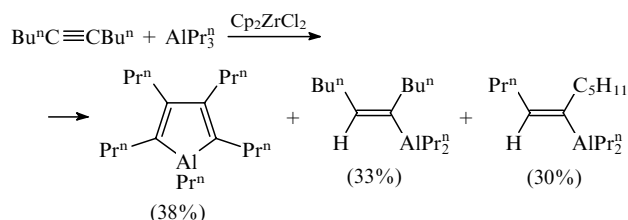


Hydroalumination of disubstituted acetylenes with Bu_3^iAl in the presence of catalytic amounts of Cp_2ZrCl_2 is accompanied by the formation of isomeric alkenylalanes, their hydrolysis affords alkenes **19** and **20** (~1:1).^{84,85} Under analogous conditions, terminal alkynes yield a mixture (~1:1) of mono- and 1,1-dialuminium compounds in practically quantitative yields.⁸⁴



(a) Bu_3^iAl , Cp_2ZrCl_2 ; (b) D_2O .

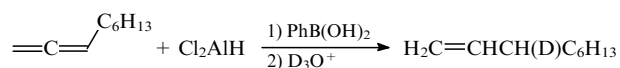
In contrast with hydroalumination with $\text{Et}_3\text{Al}-\text{Cp}_2\text{TiCl}_2$,⁸¹ the reaction of disubstituted acetylenes with Pr_3^iAl in the presence of Cp_2ZrCl_2 occurs less selectively and gives a mixture of isomeric alkenylalanes (total yield 63%) and alumacyclopentadiene (38%).⁸⁴



It should be noted that selective hydroalumination of terminal alkynes with trialkylalanes R_3Al [$\text{R} = \text{Et}, \text{Bu}^i, \text{EtCH}(\text{Me})\text{CH}_2$] does not take place if Fe or Ni complexes substituted titanium- or zirconium-containing catalysts. In this case, the alkenylalanes formed undergo further conversions; subsequent hydrolysis results in a complex mixture of alkenes, 1,3-dienes and trialkyl-substituted benzenes.^{86,87}

Hydroalumination of mono- and disubstituted acetylenes has found wide application in synthetic organic chemistry, particularly in the synthesis of practically valuable trisubstituted alkenes,⁷⁶ substituted 1,3-dienes,⁸⁸ alk-1-en-3-ynes,⁸⁹ alkenylsilanes and alkenyl sulfones,^{90,91} 1-alkyl-2-halogenocyclopropanes,⁹² *Z*-alkenes,⁹³ etc.

Hydroalumination of allenes (both thermal with Bu_2^iAlH ,⁹⁴ and that with the use of LiAlH_4 in THF in the presence of catalytic amounts of Ti or Zr complexes, e.g., Cp_2TiCl_2 , TiCl_4 , TiCl_3 , ZrCl_4 or Cp_2ZrCl_2) is non-selective.⁹⁵ This reaction may be highly regioselective with the use of HAlCl_2 in the presence of catalytic amounts of organoboranes.^{95,96}



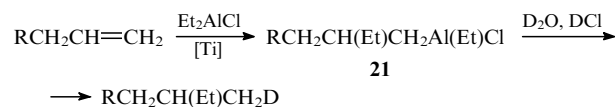
Thus in the majority of cases, stereoselective hydroalumination of alkynes and allenes occurs under mild conditions. Hydrolysis of the resulting higher alkenylalanes affords *Z*-alkenes in high yields.

IV. Carboalumination of alkenes catalysed by titanium and zirconium complexes

Catalytic carboalumination of unsaturated compounds gives an access to novel types of higher OAC. It is known⁹⁷ that carboalumination of terminal alkenes in the absence of catalysts usually occurs under drastic conditions and is accompanied by side reactions of hydro- and dehydroalumination. In the presence of metal complex catalysts, carboalumination proceeds under milder conditions and with higher selectivity.

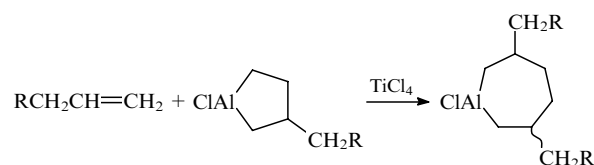
The first examples of catalytic carboalumination of alkenes aimed at the synthesis of higher dialkylhalogenoalanes were described in 1979.⁹⁸ This method is based on a consecutive insertion of ethylene at the Al–C bond in the presence of low-valent Ti complexes. This reaction results in the formation of higher OAC (dialkylaluminium chlorides) with the number of carbon atoms from 4 to 30.

The reaction of terminal alkenes with Et_2AlCl in the presence of 0.3 mol.%–3.0 mol.% $\text{Ti}(\text{O}i\text{Bu})_4$ or TiCl_4 was studied by Dzhemilev *et al.*⁹⁹ It was found that Et_2AlCl carboaluminates alkenes even at ~20 °C; this reaction proceeds with high regioselectivity and affords the corresponding higher dialkylaluminium chlorides **21** in high yields.

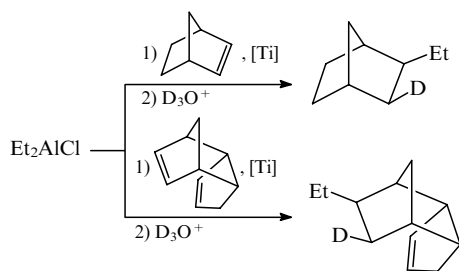


This reaction is of general character and is successfully employed in the synthesis of OAC and in directed synthesis of natural compounds.^{99–101}

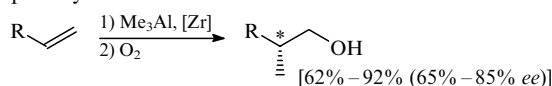
Carboalumination of terminal alkenes with 3-alkyl-1-chloroalumacyclopentanes was used to obtain other cyclic OAC, e.g., 1-chloro-3,6-disubstituted alumacycloheptanes.¹⁰²



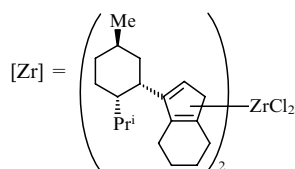
Dialkylhalogenoalanes, such as Et_2AlCl and Me_2AlCl , carboaluminate substituted norbornenes in the presence of catalytic amounts of Ti complexes [Cp_2TiCl_2 , $\text{Ti}(\text{acac})_2\text{Cl}_2$, TiCl_4] with high stereoselectivity; subsequent hydrolysis results in alkylated norbornanes.^{103,104}



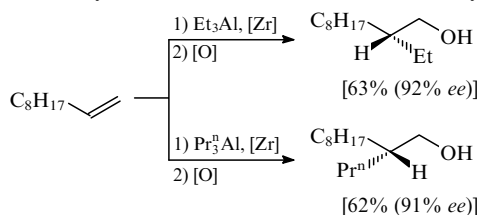
Carboalumination of terminal alkenes with Me_3Al in the presence of chiral derivatives of zirconocene, *e.g.*, bis(1-neomenthylindenyl)zirconium dichloride, bis(1-neo-isomenthyl-4,5,6,7-tetrahydroindenyl)zirconium dichloride, *etc.* with subsequent oxidation of alanes is used in a highly enantioselective synthesis of optically active alcohols.¹⁰⁵



$\text{R} = \text{C}_6\text{H}_{13}, \text{Pr}^i\text{CH}_2, \text{Ph}, \text{PhCH}_2, \text{HO}(\text{CH}_2)_4, \text{Et}_2\text{N}(\text{CH}_2)_3;$

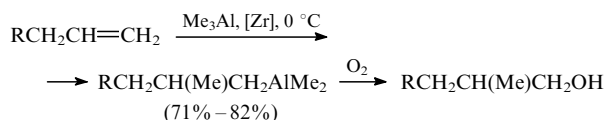


The direction of the reaction of trialkylalanes with alkenes depends on the solvent used. Thus carboalumination in 1,1-dichloroethane proceeds with high enantioselectivity in the presence of catalytic amounts of chiral zirconium catalysts.¹⁰⁶



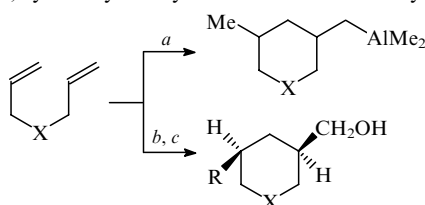
$[\text{Zr}]$, bis(1-neomenthylindenyl)zirconium dichloride.

Carboalumination of terminal alkenes with Me_3Al is selective when a two-component catalyst $\text{Cp}_2^*\text{ZrMe}_2 - \text{B}(\text{C}_6\text{F}_5)_3$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) (toluene, 0°C , ~ 3 h) is used.¹⁰⁷



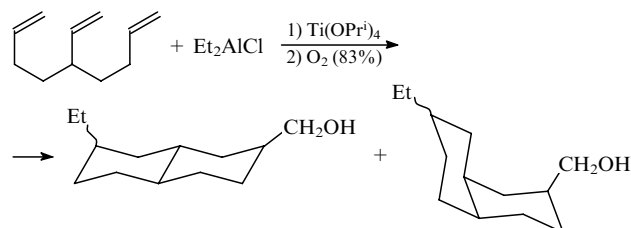
$\text{R} = \text{H}_2\text{C=C(Me)(CH}_2)_2, \text{Me(CH}_2)_2.$

In contrast with terminal alkenes, hexa-1,5-diene, hepta-1,6-diene, octa-1,7-diene and their N-, O- and Si-containing derivatives react with trialkylalanes¹⁰⁷ or dialkylhalogenoalanes¹⁰⁸ in the presence of Zr- or Ti-containing complex catalysts to give, as a rule, cycloalkylmethylalanes or their heterocyclic analogues.

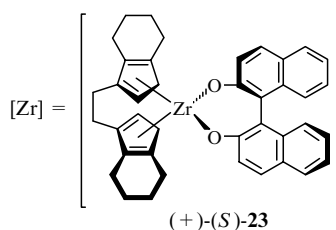
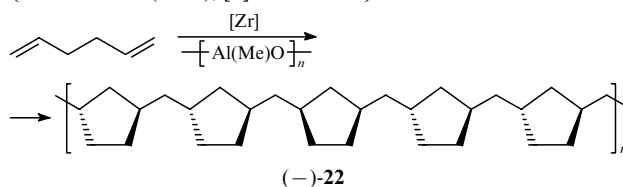


(a) Me_3Al , $\text{Cp}_2^*\text{ZrMe}_2$, $\text{B}(\text{C}_6\text{F}_5)_3$, 0°C ; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{X} = (\text{CH}_2)_n, \text{R}_2\text{Si}, \text{PhN}, \text{CHOSiR}_3$ (51%–88%); (b) R_2AlCl , $\text{Ti}(\text{OPr}^i)_4$; $\text{R} = \text{Et}, \text{Pr}^n, \text{Bu}^i$; $\text{X} = \text{CH}_2$; (c) $[\text{O}]$.

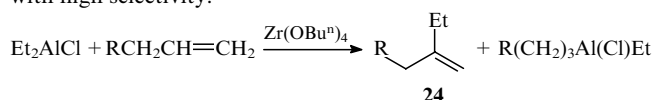
Negishi *et al.*¹⁰⁸ carried out cascade carboalumination of 5-vinylnona-1,8-diene in the presence of Et_2AlCl and $\text{Ti}(\text{OPr}^i)_4$ as a catalyst.



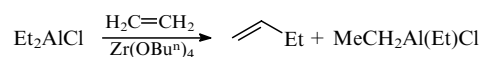
Catalytic carboalumination of non-conjugated dienes in the presence of Zr, Cp_2ZrX_2 or $\text{Cp}_2^*\text{ZrX}_2$ complexes ($\text{X} = \text{Cl}, \text{Me}$; $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) and methylalumoxane $-\text{[Al(Me)O]}_n-$ was used for diastereo- and enantioselective cyclopolymerisation of hexa-1,5-diene. The diastereoselectivity of this reaction depends on the original catalyst. Catalysis with Cp_2ZrMe_2 at -78°C results in a polymer *trans*-**22** (yield 91%), whereas in the case of $\text{Cp}_2^*\text{ZrCl}_2$ the yield of *trans*-**22** is 14% at -25°C .¹⁰⁹ Cyclopolymerisation of hexa-1,5-diene in the presence of a chiral zirconium catalyst, (+)-(*S*)-**23**, and methylalumoxane gives the chiral polymer (–)-**22** [*trans*-isomer (68%), $[\alpha] = -49.3^\circ$].^{110, 111}



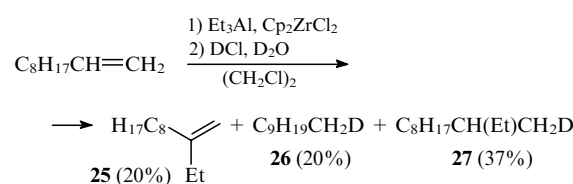
In the presence of $\text{Zr}(\text{OBu})_4$, terminal alkenes are alkylated with Et_2AlCl into position 2; alkenes **24** are formed in one step and with high selectivity.¹¹²



Ethylation of ethylene with Et_2AlCl in the presence of zirconium catalysts, *e.g.*, $\text{Zr}(\text{OBu}^n)_4$, $\text{Zr}(\text{OR})_n\text{Cl}_{4-n}$, served as the basis for the synthesis of but-1-ene.¹¹³

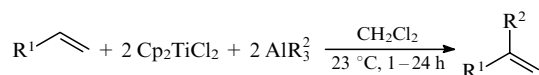


The reaction of dec-1-ene with AlEt_3 in the presence of Cp_2ZrCl_2 yields hydro- (**26**) and carboalumination (**27**) products as well as 1,1-dialkylethylenes **25**.¹⁰⁶



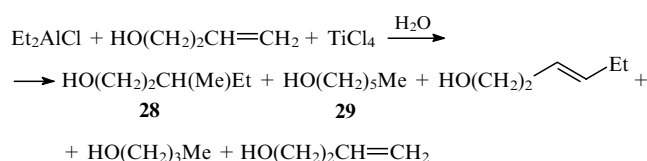
Reactions of trialkylalanes with terminal alkenes (including functionally substituted ones) in the presence of 2 equivalents of Cp_2TiCl_2 and trialkylaluminium in CH_2Cl_2 also result in 1,1-disubstituted alkenes. According to Barber *et al.*,¹¹⁴ carboalumination of alkenes under these conditions affords trialkylalanes which contain hydrocarbon radicals with an *iso*-structure;

they undergo β -hydride elimination by titanium complexes to give the corresponding alkenes in sufficiently high yields (45%–85%).

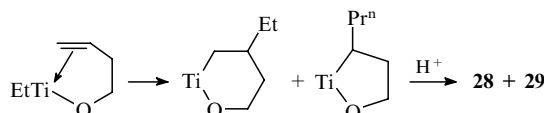


$R^1 = \text{C}_8\text{H}_{17}, \text{MeCO}_2(\text{CH}_2)_4, \text{Br}(\text{CH}_2)_4, \text{NC}(\text{CH}_2)_4; R^2 = \text{Me, Et, Bu}^n.$

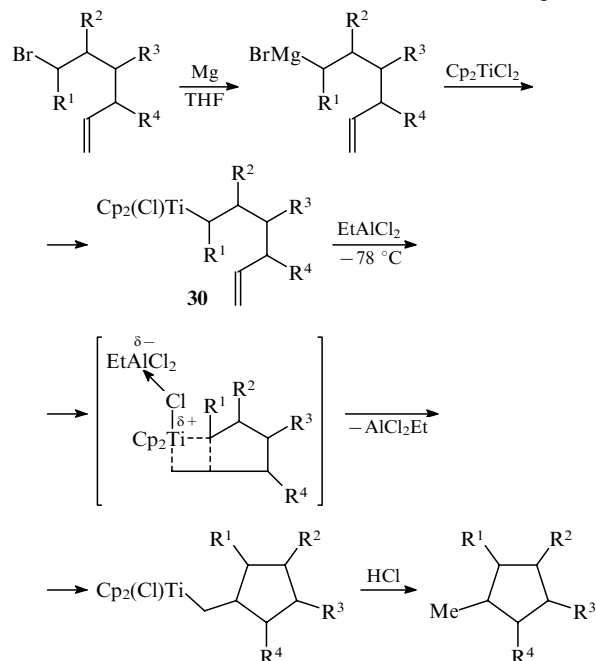
Homoallylic alcohols react with Et_2AlCl in a non-selective manner. This reaction can be accomplished only in the presence of stoichiometric amounts of Ti-containing compounds, *e.g.*, Cp_2TiCl_2 , TiCl_4 , $\text{Ti}(\text{acac})_2\text{Cl}_2$.^{114–117} Carbometallation results in two regioisomeric products (**28** and **29**) and is accompanied by side reactions, such as hydrometallation, hydrogenation, isomerisation and β -hydride elimination.



It is believed^{114–117} that the reaction of Et_2AlCl with titanium compounds results in the formation of the corresponding ethyl-titanium complexes which are active in further carbometallation of terminal alkenes. Subsequent hydrolysis affords isomeric alcohols **28** and **29**.



In a continuation of these studies, the reaction of intramolecular carbometallation in the presence of EtAlCl_2 was further extended to the selective synthesis of substituted cyclopentanes from 1-bromohex-5-enes.^{118–120} The role of EtAlCl_2 complexes consists in the activation of the intermediate titanium complex **30**.



Thus the carboalumination of alkenes with the simplest organoaluminium compounds catalysed by transition metal complexes permits simultaneous formation of C–C and Al–C bonds with high regio- and stereoselectivities. Further transformations of the organoaluminium compounds formed in the process make it possible to obtain alcohols, aldehydes, acids and other compounds.

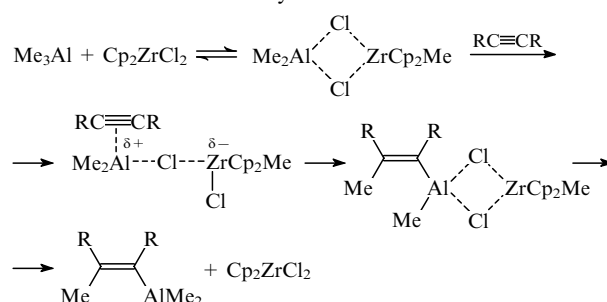
V. Carboalumination of alkynes catalysed by transition metal complexes

The reaction of gaseous acetylene with trialkylalanes occurs under mild conditions ($40\text{--}60^\circ\text{C}$) with high stereoselectivity and results in *Z*-alkenyldialkylalanes, this being one of the simplest examples of carboalumination of alkynes with OAC.⁷⁴ The features of this non-catalytic reaction and alkenylalane conversions are documented in a substantial body of literature (see, *e.g.*, Refs 18–20 and 121). Catalytic carboalumination of alkynes has been extensively generalised (*cf.*, *e.g.*, Refs 17, 47, 122–125). The present review considers the synthesis of alkenylalanes by catalytic carboalumination of alkynes with trialkyl- and halogenoalkylalanes.

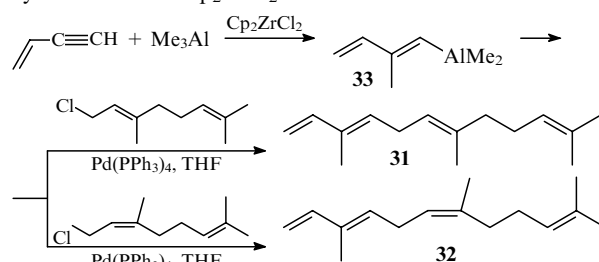
Carboalumination of mono- and disubstituted acetylenes is carried out in the presence of transition metal compounds derived from Fe,⁸⁶ Mn, Ni, Ti,^{126–130} Zr¹³¹ and Cu salts and complexes;^{132–134} this reaction utilises trialkylalanes (Et_3Al , Bu_3Al , $[\text{EtCH}(\text{Me})\text{CH}_2]_3\text{Al}$),⁸⁶ chlorodialkylalanes (Me_2AlCl ,¹³⁵ Et_2AlCl ,¹³¹ Pr^nAlCl),¹³¹ allyl-, benzylalanes¹³⁶ and alumocuprates^{132–134} as carbometallating reagents. Such reactions are generally non-selective and yield a complex mixture of regioisomers.

A two-component system proposed by Negishi *et al.*^{137–139} which contains AlMe_3 and catalytic amounts of Cp_2ZrCl_2 is one of the most efficient reagents for acetylene carbometallation presently available. Later, this system was modified by addition of H_2O .¹⁴⁰

Yoshida and Negishi¹⁴¹ have initially proposed that Cp_2ZrCl_2 -catalysed carboalumination of alkynes involved methylation of Cp_2ZrCl_2 with trimethylaluminium to give MeZrCp_2Cl and Me_2AlCl . Subsequent carbocyclozirconation of the alkyne yields the corresponding alkenylzirconium derivatives; their transmetalation with Me_2AlCl results in alkenyldimethylalanes with simultaneous regeneration of the catalyst. The reaction mechanism included the existence of a reversible reaction where the methyl group or the methyl radical is transferred from the Al atom to the Zr atom as can be evidenced from the NMR data. However, further investigations^{142, 143} showed that this reaction involves direct carboalumination of alkynes.

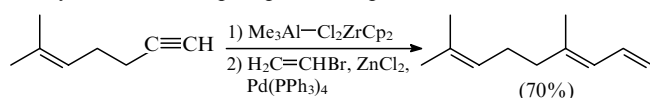


Carboalumination of alkynes resulted in a great number of practically important organoaluminium and organic compounds. Thus an elegant method was proposed for the synthesis of isoprene linear trimers **31** and **32** by stereo- and regiospecific cross-coupling of geranyl and neryl chlorides with alkadienylaluminium **33**.¹⁴⁴ The reagent **33** was synthesised by carboalumination of vinylacetylene with trimethylaluminium in the presence of catalytic amounts of Cp_2ZrCl_2 .

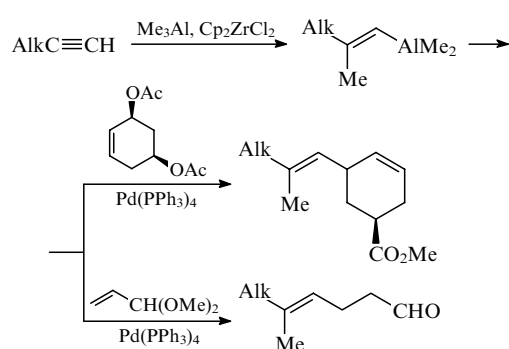


Catalytic carboalumination of terminal alkynes with AlMe_3 with subsequent functionalisation of the alkenylalanes formed was used for the synthesis of natural isoprenoids, *e.g.*, geraniol,¹⁴⁵ monocyclofarnesol¹⁴⁶ and farnesol.¹⁴⁷

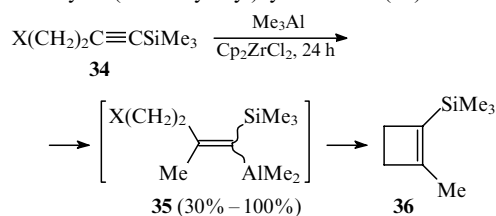
An efficient procedure has been developed for the synthesis of polyenic hydrocarbons of different structure (including those containing conjugated double bonds) using alkenylalanes and catalytic amounts of phosphine complexes of Ni or Pd.¹⁴⁸



A similar approach was used in the synthesis of cyclic and acyclic functionally substituted unsaturated compounds.^{149, 150}

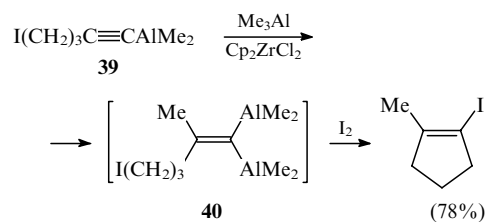
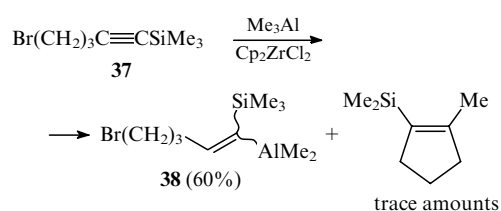


The ability of alkenylalanes to enter into the cross-coupling reactions with organic halides was used as the basis for a new method of synthesis of substituted cyclobutenes. Thus carboalumination of silylated alkynes **34** with trimethylaluminium under mild conditions yields alkenylalanes **35** containing a good leaving group X. Intramolecular cyclisation of the intermediates **35** results in 1-methyl-2-(trimethylsilyl)cyclobutene (**36**).¹⁵¹

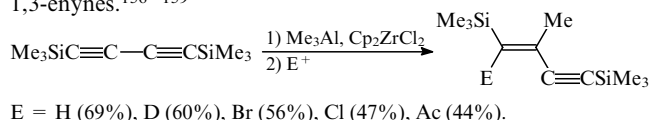


X = Cl, Br, I, OTs.

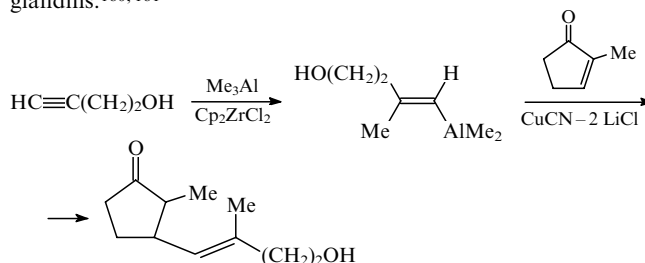
Carbometallation of ω -halogen-substituted 1-trimethylsilylalk-1-ynes or enynes with alkyl derivatives of Al, Zn or Li followed by intramolecular cyclisation of the organometallic compounds formed allows one to synthesise substituted cycloalkenes in high yields.^{152–154} 5-Bromo-1-trimethylsilylpent-1-yne (**37**) is the least prone to intramolecular cyclisation; it generates alkenylalane **38** in 60% yield. The iodo-substituted alkynylalane **39** enters into the carboalumination reaction to give the dialuminium derivative **40**; treatment of the latter with I_2 gives iodo-substituted cyclopentene.¹⁵⁵



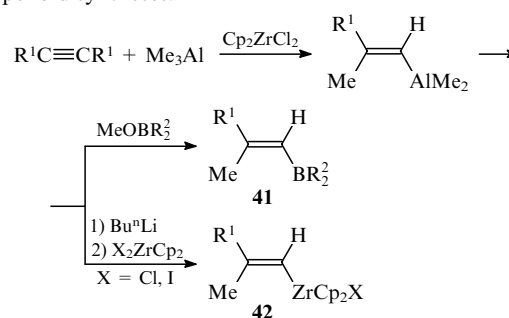
Cp_2ZrCl_2 -Catalysed carboalumination of mono- and disubstituted acetylenes or 1,3-diynes is an example of an efficient regio- and stereoselective synthesis of trisubstituted alkenes, homoallylic alcohols, esters of α,β -unsaturated acid and 1,4-disilylated 1,3-enynes.^{156–159}



Alkenylalanes obtained by carboalumination of alkynes are extremely useful for introducing alkenyl groups into the β -position of cyclic enones. This approach was used, for example, in the preparation of key compounds for the synthesis of prostaglandins.^{160, 161}



Transmetalation of alkenylalanes with organoboron or organozirconium compounds occurs under mild conditions (25 °C, 1 h) and affords the corresponding alkenylboron- (**41**) or -organozirconium (**42**) compounds which can further be used in terpenoid syntheses.¹⁶²

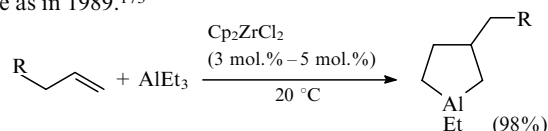


In recent years, catalytic carboalumination of alkynes has found wide application in the synthesis of natural and biologically active compounds, *e.g.*, brassinolide,¹⁶³ milbemycin,^{164–166} zoapatanol,¹⁶⁷ mabcen fragments,¹⁶⁸ synthetic precursors of lophotoxin and pukalide,¹⁶⁹ mokupalide,¹⁷⁰ trichoverrol B,¹⁷¹ verrucarins,¹⁷² *etc.*

VI. Cycloalumination of alkenes in the presence of zirconium- and titanium-containing catalysts

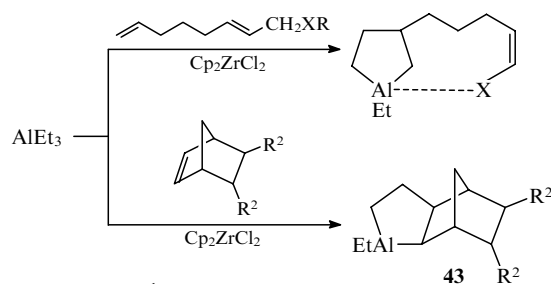
The methods developed in the late 1980's dealt mainly with the synthesis of alkyl-, cycloalkyl-, alkenyl- and vinylalanes. Data on the possibility of preparative synthesis of stable three- and five-membered OAC were practically absent in the literature. The first report on a regioselective synthesis of previously unknown five-

membered OAC (alumacyclopentanes, ACP) was published as late as in 1989.¹⁷³



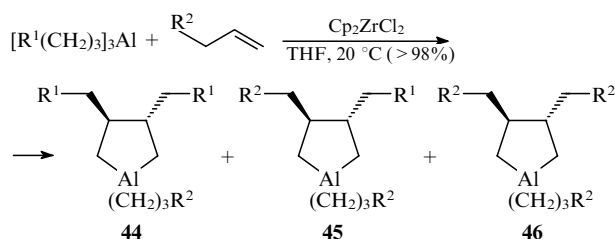
Later, it was found that this reaction is versatile and allows one to perform a one-step synthesis of five-membered OAC from AlEt_3 and terminal alkenes in nearly quantitative yields. This reaction was termed as ‘catalytic cycloalumination of unsaturated compounds’^{174–177} or ‘cyclic carboalumination’.^{84, 178}

O-, *N*- and *S*-containing alkenes and norbornenes also undergo cycloalumination to give the corresponding ACP.^{179, 180} The cycloalumination of norbornenes is highly selective and results in the formation of five-membered metallocycles **43** having an *exo*-configuration.¹⁷⁹

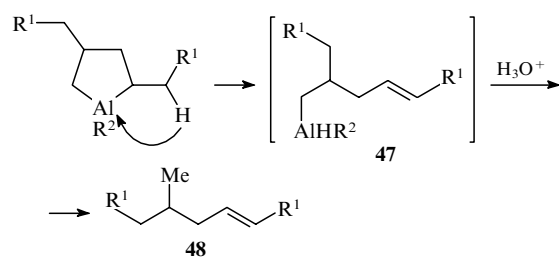


$\text{X} = \text{OR}^1, \text{SR}^1, \text{NR}^1$.

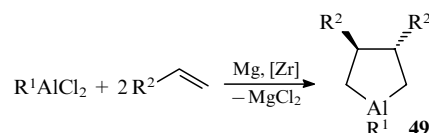
Substitution of higher OAC for AlEt_3 affords predominantly *trans*-3,4-disubstituted ACP **44–46**.¹⁸¹



This is accompanied by the formation of 2,4-dialkyl-substituted alumacyclopentanes (5%–12%); the latter undergo intramolecular β -hydride conversions into *E*-alkenylalanes **47** and, after hydrolysis, into *E*-alkenes **48**.¹⁸¹



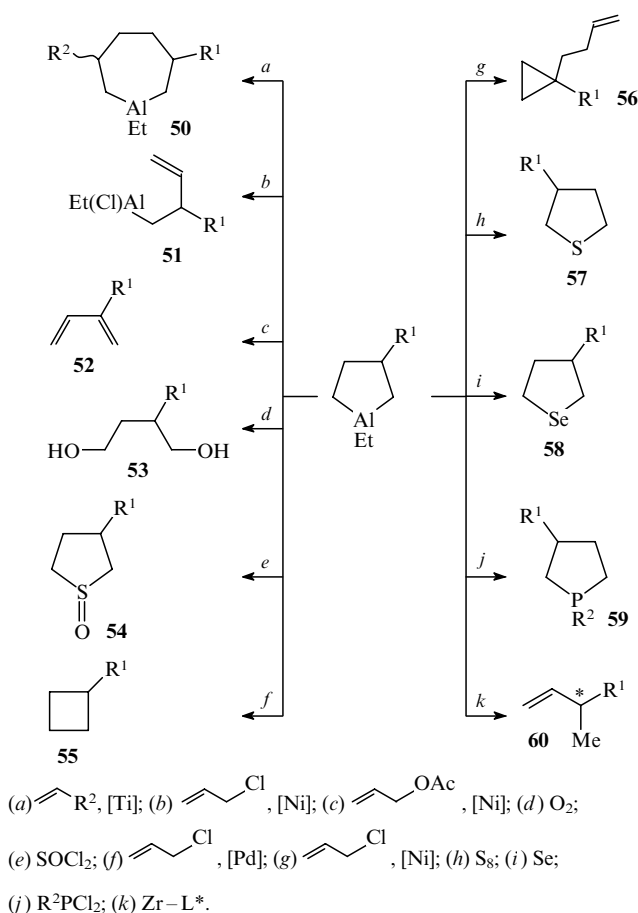
After substitution of dihalogenoalanes for higher trialkylalanes, the cycloalumination of terminal alkenes occurs more selectively and gives *trans*-3,4-dialkyl-substituted ACP. In contrast with previously developed procedures;^{173, 179, 180} the reactive catalytic intermediate, *viz.*, Cp_2Zr , is generated in these reactions by reduction of Cp_2ZrCl_2 in THF by Mg activated with RAlCl_2 . This approach enables the synthesis of 1-alkyl-, 1-alkoxy-, 1-dialkylamino- and 1-halogeno-*trans*-3,4-dialkyl-substituted alumacyclopentanes **49** from α -alkenes, dihalogenoalanes and metallic magnesium (which is a halogenide ion acceptor) in the presence of catalytic amounts of Cp_2ZrCl_2 or ZrCl_4 (yields 70%–90%).^{182–184} The structure of substituted alumacyclopentanes, the position of substituents and their configuration were established by spectral methods.^{185, 186}



$\text{R}^1 = \text{Alk, RO, R}_2\text{N}$; $\text{R}^2 = \text{Alk}(\text{C}_3\text{--C}_{20})$; $[\text{Zr}] = \text{Cp}_2\text{ZrCl}_2, \text{ZrCl}_4$.

The incorporation of an alkene molecule into the Al–C bond of 3-alkyl-substituted ACP in the presence of Ti complexes is an efficient procedure for obtaining 1-ethyl-3,6-dialkyl-substituted alumacycloheptanes **50**.¹⁰² The cleavage of the Al–C bond in ACP in the presence of nickel catalysts results in the unsaturated OAC **51**¹⁸⁷ or 2-alkyl-substituted 1,3-dienes **52** in quantitative yields (Scheme 2).¹⁸⁸

Scheme 2

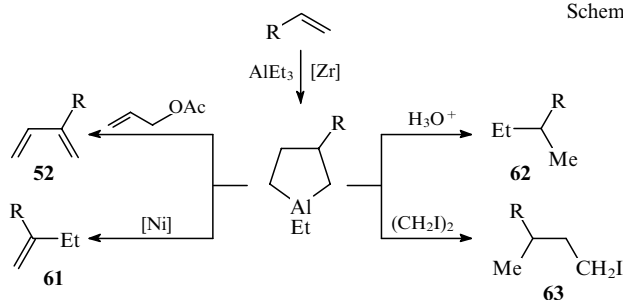


ACP was used in the synthesis of different classes of compounds (see Scheme 2). They are active co-catalysts in co-telomerisation reactions as well as in one-pot conversions of α -alkenes into 1,4-butanediols **53**,¹⁸⁹ thiolane 1-oxides **54**,¹⁹⁰ cyclobutanes **55**,^{191, 192} cyclopropanes **56**,¹⁹³ thiophanes **57**, selenophanes **58**,^{194, 195} phospholanes **59**,¹⁹⁶ α,ω -dienes¹⁹⁷ and optically active hydrocarbons **60**.¹⁹⁸

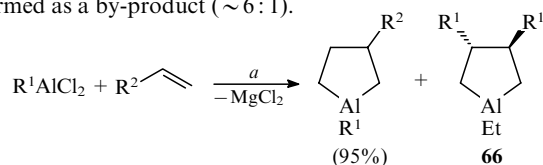
ACP were used as intermediates in preparative syntheses of 2-alkyl-substituted 1,3-dienes **52** (β -vinylation¹⁸⁸), 1,1-dialkylethylenes **61** (reductive β -vinylation^{187, 199}), branched hydrocarbons **62** (reductive β -ethylation²⁰⁰) and iodo-derivatives **63** (reductive β -iodoethylation²⁰¹) from alkenes (Scheme 3).

The use of ACP offers a simple approach to the synthesis of linear *E*-isoprenoids **64** and **65** with a definite number of the C_5 fragments.²⁰² Alumacyclopentanes can be used in the synthesis of biologically active compounds, *e.g.*, pheromones of pine sawfly, German cockroach and mealworms *Tribolium confusum* and *Tribolium castaneum* (Scheme 4).^{203–206}

Scheme 3

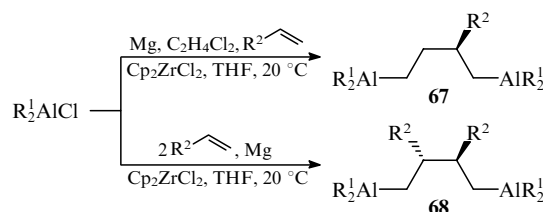


A method for the synthesis of 3-alkyl-substituted ACP from α -alkenes and AlEt_3 (see Refs 173, 179, 180) was recently modified through the application of more readily available and less pyrophoric reagents. This novel procedure is also based on the *in situ* generation of an active catalytic species, *viz.*, Cp_2Zr , from Cp_2ZrCl_2 and simultaneous introduction of α -alkene and ethylene molecules, synthesised *in situ* from dichloroethane and metallic Mg, into the coordination sphere of the central atom of the catalyst.^{207,208} The main product of this reaction is 3-alkyl-substituted ACP; 1-ethyl-*trans*-3,4-dialkyl-substituted ACP **66** is formed as a by-product ($\sim 6:1$).



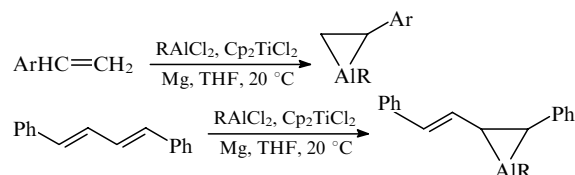
(a) Cp_2ZrCl_2 , Mg, $\text{C}_2\text{H}_4\text{Cl}_2$, THF, 20°C .

Substitution of R_2AlCl for RAlCl_2 gives substituted 1,4-dialuminiobutanes **67** and **68** which represent a novel class of acyclic OAC. This reaction was studied rather comprehensively for numerous α -alkenes and structurally different OAC.²⁰⁹

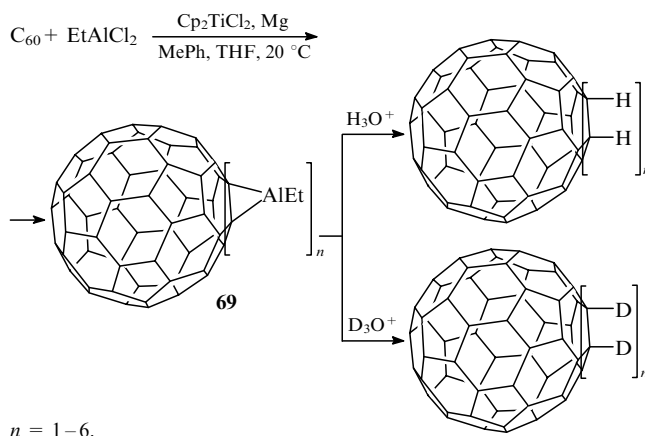


$\text{R}^1 = \text{OR}^3, \text{NR}_2^3, \text{R}^3\text{S}, \text{Alk}(\text{C}_3-\text{C}_{20})$.

In 1997, Dzhemilev *et al.* developed a method for the synthesis of a previously unknown class of metallacycles, *viz.*, alumacyclopropanes. Cycloalumination of arylalkenes (styrene, *o*- and *p*-methylstyrene and 1,4-diphenylbuta-1,3-diene) with ethylaluminum dichloride in the presence of metallic magnesium as a chloride ion acceptor and Cp_2TiCl_2 yielded alumacyclopropanes (yields 80%).²¹⁰

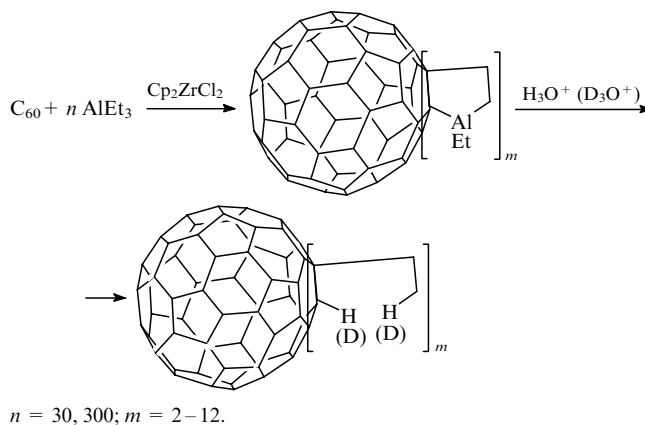


Treatment of the C_{60} fullerene with EtAlCl_2 in the presence of Cp_2TiCl_2 and Mg yielded the organometallic compounds **69** containing alumacyclopropane fragments.^{207,211} Cycloalumination of C_{60} probably involves titanacyclopropane intermediates, $\text{Cp}_2\text{Ti}(\eta^2-\text{C}_{60})$;²¹² transmetalation of the latter with EtAlCl_2 results in fullerenic alumacyclopropanes **69**.



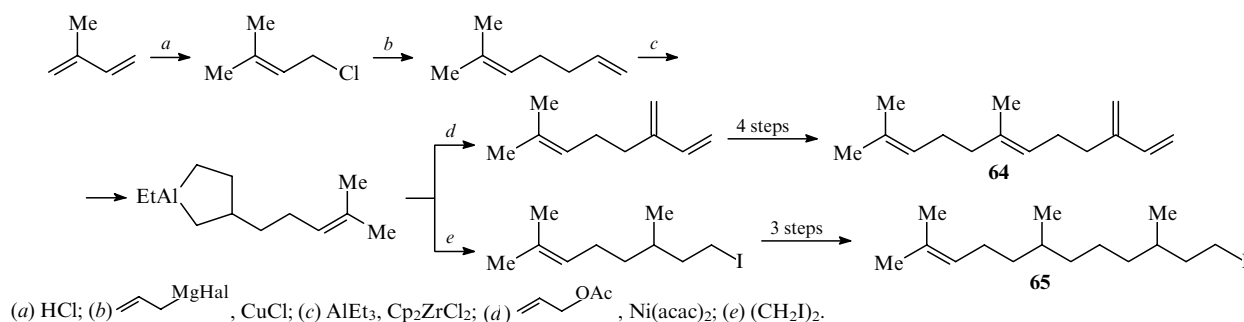
$n = 1-6$.

Cp_2ZrCl_2 -Catalysed cycloalumination of the C_{60} fullerene with AlEt_3 recently carried out by Dzhemilev *et al.*^{213,214} gave the organometallic derivatives of C_{60} containing alumacyclopentane fragments. Organometallic fullerene derivatives containing two alumacyclopentane fragments are formed in toluene ($\sim 22^\circ\text{C}$, 36 h) at the $\text{C}_{60}:\text{AlEt}_3$ ratio of 1:30 (total yield $\sim 80\%$). At the $\text{C}_{60}:\text{AlEt}_3$ ratio of 1:300, up to 12 alumacyclopentane fragments can be introduced into the C_{60} molecule.

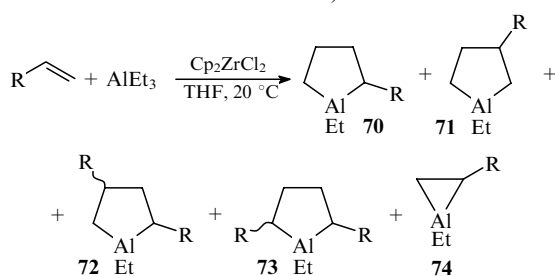


$n = 30, 300; m = 2-12$.

Scheme 4

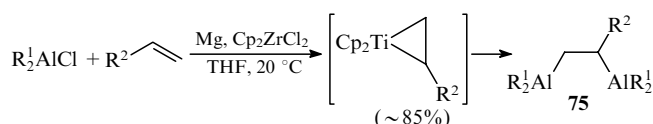


In contrast with aliphatic alkenes, cycloalumination of terminal aryl-substituted alkenes with AlEt_3 in the presence of Cp_2ZrCl_2 occurs less selectively. Thus a mixture of mono- and disubstituted arylalumacyclopentanes and 2-aryl-1-ethylalumacyclopentane are formed in a total yield > 90% (**70**:**71**:**72**:**73**:**74** ~ 50:25:15:3:7).^{207, 215}



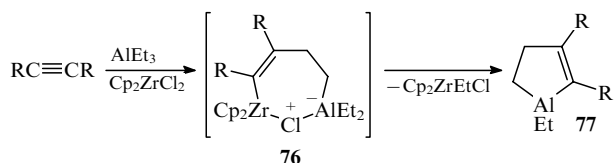
$\text{R} = \text{Ph}, 2\text{-MeC}_6\text{H}_4, 4\text{-MeC}_6\text{H}_4$.

The reaction of R_2AlCl with arylalkenes catalysed by Cp_2TiCl_2 was used in the synthesis of 1,2-dialuminomethanes **75**.²¹⁵



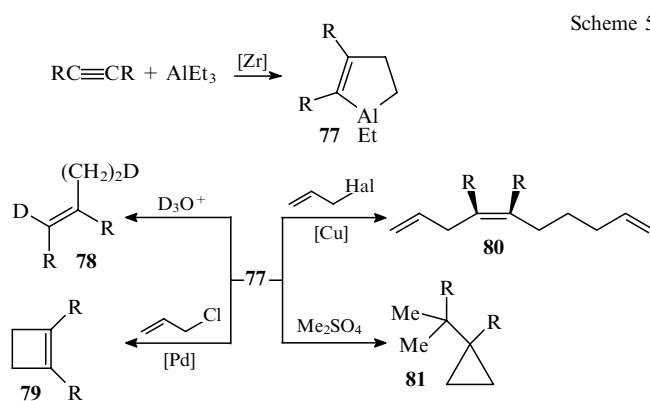
VII. Catalytic cycloalumination of alkynes

Simple procedures have been developed for the synthesis of unsaturated cyclic OAC from saturated three- and five-membered cyclic OAC in the presence of titanium- and zirconium-containing metal complex catalysts. Thus cycloalumination of disubstituted acetylenes with triethylaluminium in the presence of catalytic amounts of Cp_2ZrCl_2 gave 2,3-dialkyl(aryl)-substituted alumacyclopent-2-enes **77**.^{216, 217} Carboalumination of disubstituted acetylenes in halogen-containing solvents yields acyclic alkenylalanes.⁸⁴ The nature of the solvent plays a crucial role in the formation of intermediate titanium- and zirconium-containing metallacycles **76**, the key intermediates in the synthesis of alumacyclopentenes **77**.^{84, 218}

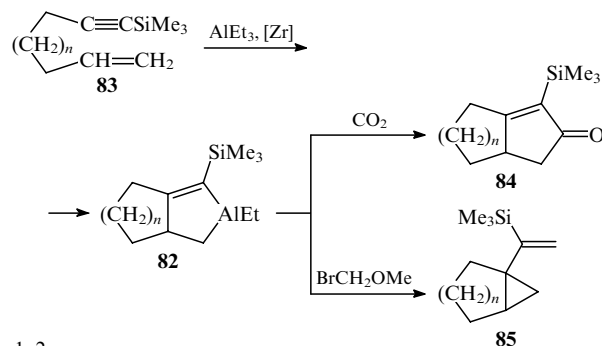


The structure of alumacyclopentenes **77** was established by spectral methods²¹⁷ and by their conversions. Thus hydrolysis of compounds **77** with D_2O gave trisubstituted alkenes **78** (Scheme 5).²¹⁷ Dealumination of OAC **77** in the presence of catalytic amounts of palladium phosphine complexes results in 1,2-disubstituted cyclobutenes **79**.²¹⁹ In the presence of an excess of dimethyl sulfate, compounds **77** are readily transformed into 1,1-dialkyl-substituted cyclopropanes **81**. Cross-coupling of OAC **77** with allyl halides results in 4,5-disubstituted 1,4(Z),9-decatrienes **80** (see Scheme 5).²²⁰

In 1998, Negishi *et al.*¹⁷⁸ carried out the synthesis of bicyclic alumacyclopentenes **82** by intramolecular cycloalumination of enynes **83** in the presence of catalytic amounts of Cp_2ZrCl_2 .

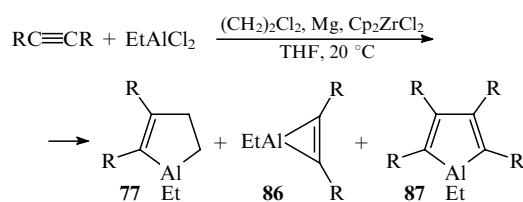


Subsequent treatment of OAC **82** with CO_2 or BrCH_2OMe resulted in the corresponding cyclopentenones **84** and vinylcyclopropanes **85**.

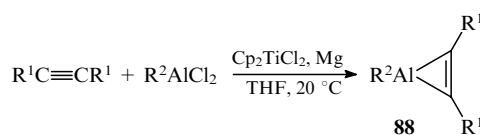


$n = 1, 2$.

A modified procedure for the synthesis of 1-ethyl-2,3-dialkyl(aryl)alumacyclopent-2-enes **77** from disubstituted acetylenes and ethylene generated *in situ* from dichloroethane and activated metallic magnesium has been recently developed by Ramazanov *et al.*^{221, 222} This reaction yields the corresponding alumacyclopentenes **86** and alumacyclopentadienes **87** as by-products (5%–30%).



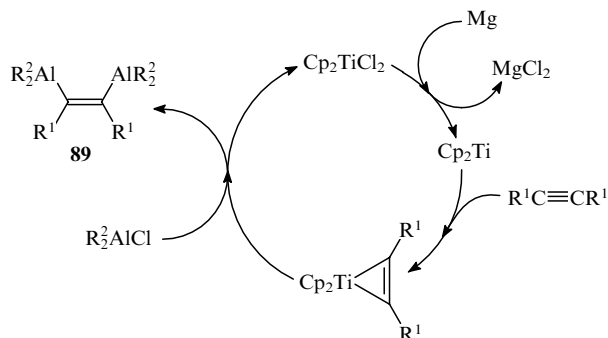
The synthesis of alumacyclopentenes **88** by cycloalumination of 1,2-disubstituted acetylenes using alkyl-dichloroalanes²²³ in the presence of Ti complexes is one of the most substantial achievements in the synthesis of small alumacycles. Presumably, these reaction conditions favour the generation of titanacyclopentene intermediates,^{224–235} their transmetalation with dihalogenoalanes results in the corresponding trisubstituted alumacyclopentenes **88**.^{223, 236–238}



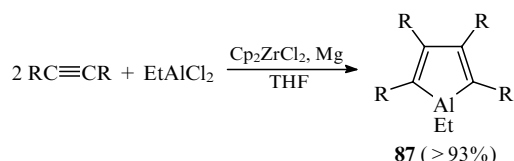
$\text{R}^1 = \text{Alk}, \text{Ph}; \text{R}^2 = \text{Alk}, \text{OR}^3, \text{NR}_2^3$.

In contrast with 1,2-disubstituted acetylenes, terminal alkynes react with AlCl_3 in the presence of Ti complexes less selectively. This reaction yields alumacyclopentadienes **87** along with alumacycloprenes **88**.

The synthesis of 1,2-dialuminoethylenes **89** by the reaction of 1,2-disubstituted acetylenes with R_2AlCl under the action of catalytic amounts of Cp_2TiCl_2 in the presence of a chloride ion acceptor (activated Mg) has been carried out by Dzhemilev *et al.*²³⁹



1-Ethyl-2,3,4,5-tetraalkyl-1-alumacyclopenta-2,4-dienes **87** were synthesised with high selectivity by cycloalumination of 1,2-dialkyl-substituted acetylenes using EtAlCl_2 in the presence of Cp_2ZrCl_2 (5 mol.%, $\sim 23^\circ\text{C}$, TTF).^{221,240} The content of alumacycloprenes in the reaction mixture does not exceed 5%–7%.



$\text{R} = \text{Alk}(\text{C}_3 - \text{C}_{10})$.

VIII. Conclusion

In the past 10–15 years, organoaluminium compounds have gained popularity in the practice of synthetic organic and organometallic chemistry along with organomagnesium reagents.

The catalytic reactions of hydro-, carbo- and cycloalumination of alkenes, dienes and alkynes are carried out under mild conditions and yield OAC with high regio- and stereoselectivity. Thus OAC were used in the synthesis of the major classes of natural compounds, such as vitamins, antibiotics, alkaloids, steroids, carbohydrates, prostaglandins, isoprenoids, drugs, *etc.*

We are convinced that future syntheses will widely employ organoaluminium compounds and will be aimed at obtaining novel co-catalysts for oligomerisation and polymerisation reactions and efficient reagents for regio- and stereoselective reduction and alkylation of unsaturated compounds as well as at the development of non-traditional approaches to the design of organic and organometallic compounds and most advanced chemical technologies.

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Dehydrocondensation of organylsilanes giving Si—Si bonds

V B Pukhnarevich, M G Voronkov, L I Kopylova

Contents

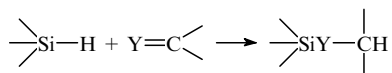
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Abstract. The data on catalytic dehydrocondensation of organylsilanes with the formation of Si—Si bonds are systematised and generalised. The mechanism and general features (the effects of the nature of the reactants and the catalyst, the solvent and the reaction conditions) of these reactions catalysed by cyclopentadienyl complexes of transition metals are considered. Electrochemical and other procedures for the dehydrocondensation of organylsilanes are discussed. The bibliography includes 220 references.

I. Introduction

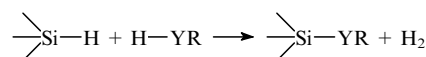
Organosilicon compounds with Si—H bonds, in particular, organylsilanes of the $R_{4-n}SiH_n$ type ($n = 1-3$), are highly reactive substances.¹ In this connection, these compounds are of considerable theoretical and practical interest.

Thus addition of silanes to unsaturated substrates containing the C=C, C=N, N=N, C=O, C≡C or N≡N bonds, *viz.*, hydrosilylation,² is one of the most important procedures for the synthesis of various organosilicon compounds.¹⁻⁸ This unique reaction makes it possible to form Si—C bonds as well as Si—O—C and Si—N—C groups in one stage.



Y = R_2C , O, HN *etc.*

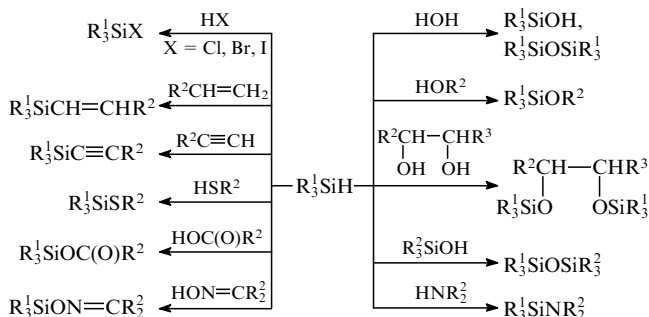
Organylsilanes, unlike their formal analogues, *viz.*, hydrocarbons, readily enter into dehydrocondensation reactions with OH, NH, SH and CH acids. Dehydrocondensation reactions with different compounds, such as water, alcohols, phenols, inorganic and carboxylic acids, amines, thiols, *etc.*, have been well studied.



Y = O, S, NH; R = H, Alk, Ar, Ac *etc.*

Hydrosilylation and dehydrocondensation are most often catalysed by transition metal compounds and nucleophiles. Examples of the use of dehydrocondensation of organylsilanes for the preparation of organosilicon compounds are shown in Scheme 1.

Scheme 1



Synthetic applications of dehydrocondensation of silanes with hydroxy-containing organic compounds and the mechanism of this reaction have been adequately surveyed in the reviews.^{1,9-14} Of more recent investigations, studies on alcoholysis of mono-, di- and trisubstituted silanes with saturated and unsaturated primary and secondary alcohols and diols in the presence of complexes of copper $\{[Ph_3PCuH]_6\}$,¹⁵ titanium¹⁶ and manganese $\{[Mn(CO)_4Br]_2\}$ ¹⁷ as well as in the presence of soluble platinum, palladium, nickel, ruthenium and rhodium complexes fixed on silica gel,¹⁸⁻²⁰ and studies on alcoholysis of disilanes in the presence of tetrabutylammonium fluoride²¹ are worthy of note.

Dehydrocondensation of silanes with phenols, ammonia, amines, thiols and carboxylic acids are less well understood.¹¹ Of the recent advances, phenolysis catalysed by potassium fluoride^{22,23} and ammonolysis (with ammonia or hydrazines) of phenylmethyl-, diphenylmethyl- and methyldichlorosilanes in the presence of dimethyltitanocene²⁴⁻²⁷ should be mentioned. The synthesis of quaternary ammonium difluorosilicates by the reactions of $R_2^1R^2SiH$ with $R_3^2R^4N^+HF_2^-$ was reported.²⁸ The reactions of unsaturated organic acids with dimethylchlorosilane followed by intramolecular hydrosilylation of the resulting β,γ -unsaturated acyloxysilanes catalysed by Pt(II) 1,5-cyclooctadiene (COD) complexes afford silaoxacyclopentanones. The latter can

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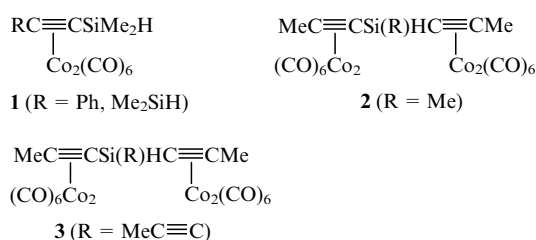
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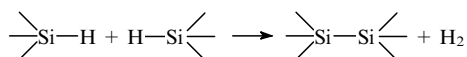
be converted into esters of hydroxycarboxylic acids. This method was used in the stereoselective synthesis of methyl ester of (2*S*,3*R*)-3-hydroxy-*N*-Boc-proline.²⁹ Products of hydrosilylation of styrene, 1-octyne and phenylacetylene with phenyl- and diphenylsilane enter into dehydrocondensation reactions with arenethiols ArSH (Ar = Ph, 4-MeC₆H₄ or 4-MeOC₆H₄) in the presence of rhodium tris(triphenylphosphine) chloride.³⁰

Dehydrocondensation of octacarbonyldicobalt complexes of mono-, di- and triethynylsilanes (**1–3**) in the absence of nucleophilic or metal complex catalysts occurs through interactions between the Si–H bond and water, alcohols, carboxylic acids, primary amines, *etc.*^{31, 32}



Dehydrocondensation of silanes with CH acids (alkanes, alkenes, alkynes and their derivatives) has been studied in sufficient detail.^{11, 33–39}

Dehydrocondensation of organosilicon compounds containing Si–H bonds to form disilanes has remained poorly studied for a long time and attracted considerable attention only recently.



Organosilicon compounds containing Si–Si bonds have attracted growing interest because they can be used as starting compounds in the synthesis of organic and inorganic derivatives of oligo- and polysilanes possessing specific structural, electronic, optical and chemical properties.^{40, 41} These oligo- and polysilanes find use in the production of ceramic materials,^{42–64} semiconductors,^{4, 42, 48, 49, 65–69} photoresistors,^{42, 44, 46, 48, 49, 70–77} photoinitiators of polymerisation of alkenes, *etc.*⁴²

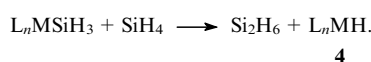
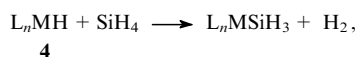
In this review, studies on dehydrocondensation of organylsilanes (which is sometimes wrongly called ‘dehydropolymerisation’⁴²) accompanied by the formation of Si–Si bonds are surveyed.

II. Catalytic dehydrocondensation of organylhydrosilanes

1. Catalysis by compounds of Group IIIB elements

The data on the use of complex compounds of Group IIIB elements as catalysts of dehydrocondensation of silanes are scarce.

The activation energies and the enthalpies of dehydrocondensation of monosilane in the presence of complexes of lanthanides M (M = Sc, Y, La, Lu or Sm), which were calculated in a study,⁷⁸ indicate that this reaction can in principle proceed. It is believed that the first stage of the process involves silylation of intermediate **4**. The second stage leads to the formation of disilane and regeneration of intermediate **4**.

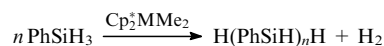


Of Group IIIB elements, only derivatives of lanthanides and actinides, as far as is known, are active in dehydrocondensation.^{78–80} Thus PhSiH₃ in the presence of Cp^{*}₂NdCH(SiMe₃)₂ (Cp^{*} = η⁵-C₅Me₅) was converted into oily polyphenylsilane with a molecular weight (*M*) of 600 at 80 °C during two days.⁸⁰

The dimeric hydride complex of lanthanocene [Cp^{*}₂LaH]₂ is also an active catalyst of dehydrocondensation of phenylsi-

lane.^{80, 81} In this case, a mixture of PhSiH₂SiH₂Ph and (PhSiH₂)₂SiHPh was formed from PhSiH₃.

Cyclopentadienyl complexes of actinides also catalyse dehydrocondensation of organylsilanes. Thus cyclopentadienyl derivatives of dimethyluranium and dimethylthorium converted phenylsilane into 1,2-diphenyldisilane (M = Th) or an oligomer (M = U) in 70% and 30% yields, respectively, even at room temperature during 6 h.⁸²



M = U, Th.

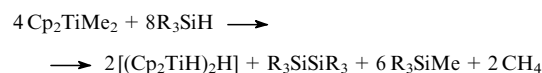
Dimethylmetallocenes, which are actinide derivatives, rank below isostructural titanocenes and zirconocenes in the catalytic activity.⁸²

Dehydrocondensation of silanes of the Si_aH_bR_c¹ type [R¹ = Alk, Ar, alkenyl, AlkO, Hal or NHR²; *a* ≥ 2; *b* ≥ 1; (*b* + *c*) = (2*a* + 2)] occurs under an inert atmosphere in the presence of Cp₂MR₂³ (M = Th or U).^{83–85}

2. Catalysis by compounds of Group IVB elements

a. Catalysis by alkyl- and arylmetallocenes CpMR₃, Cp₂MR₂ and Cp₂MPh₂

Dehydrocondensation of silanes, such as PhSiH₃, MeSiH(OR)₂ and HSi(OR)₃, in the presence of dimethyltitanocene was first reported by Harrod and coworkers in 1984.⁸⁶ The above-mentioned silanes react with dimethyltitanocene in a hydrocarbon solvent or without a solvent at room temperature to give the titanium hydride complex and the corresponding disilane derivatives.



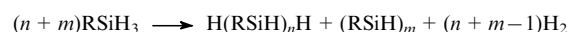
Trialkyl- and triarylsilanes as well as chlorosilanes do not undergo dehydrocondensation even at 80–120 °C.^{82, 86, 87}

More recently, Harrod and coworkers published a series of studies^{82, 88–100} on dehydrocondensation of monosubstituted silanes (RSiH₃, where R = Ph, Bn or C₆H₁₃), disubstituted silanes (R¹R²SiH₂, where R¹ = R² = Ph or R¹ = Ph and R² = Bu), trialkoxysilanes (RO)₃SiH (R = Me or Et), Me(EtO)₂SiH and 1,3,5,7-tetramethylcyclotetrasilane catalysed by dialkyltitanocenes Cp₂MR₂ (M = Ti or Zr; R = Me or Bn but not Ph). Later on, the series of catalysts of dehydrocondensation of silanes was substantially extended. It was demonstrated^{82, 89–91} that mono-(cyclopentadienyl)trialkyl and di(cyclopentadienyl)dialkyl derivatives of Group IVB metals (Ti, Zr and Hf) exhibit a high catalytic activity in this reaction.

The most important advantage of the above catalysts over inorganic compounds,^{24, 29, 101–107} complex and organometallic compounds^{108, 109} is their ability to catalyse the formation of oligomers containing 10–20 silicon atoms in the chains under rather mild conditions (Table. 1).

The catalytic activity of sterically hindered (cyclopentadienyl)trimethyltitanium as well as of its zirconium analogue in dehydrocondensation of phenylsilane is low.⁸² Attempts to perform dehydrocondensation of phenylsilane in the presence of Cp₂HfMe₂ at 20 or 90 °C (12 h) were unsuccessful.

Generally, dehydrocondensation of silanes RSiH₃ catalysed by dimethyltitanocene or dimethylzirconocene affords a mixture of linear and cyclic oligomers the ratio of which depends on the nature of the initial silane and the reaction conditions.^{92, 93, 112}



Thus phenylsilane forms predominantly linear oligomers, whereas hexylsilane produces a mixture of linear and cyclic oligomers. In the presence of dimethyltitanocene, benzylsilane was converted predominantly into hexabenzylcyclohexasilane (the yield was ~ 35%).⁹²

Table 1. Comparative catalytic activities of metallocenes of derivatives of Groups IV – VII elements in dehydrocondensation of organylhydrosilanes RSiH₃ and R₂SiH₂.

R ₄ – <i>n</i> SiH _{<i>n</i>}	Catalyst	<i>T</i> / °C	<i>t</i> / h	Reaction products	Yield (%)	Average molecular weight		Ref.
						<i>M</i> _n	<i>M</i> _w	
PhSiH ₃	(MeCp) ₂ TiMe ₂	20	6	H(SiHPh) _{<i>n</i>} H	85	—	—	82
	(MeCp) ₂ ZrMe ₂	20	6	H(SiHPh) _{<i>n</i>} H	100	—	—	82
	CpCp*TiMe ₂	20	40	H(SiHPh) _{<i>n</i>} H	80	—	—	82
	[CpCp*ZrH ₂] ₂	23	0.25	H(SiHPh) _{<i>n</i>} H	11	2430	8360	48
	[CpCp*ZrH ₂] ₂	23	15	H(SiHPh) _{<i>n</i>} H	14	2300	11 950	48
	CpCp*ZrMe ₂	20	40	H(SiHPh) _{<i>n</i>} H	100	—	—	82
	CpCp*ZrMe ₂	23	24	H(SiHPh) _{<i>n</i>} H	—	1700	6100	48
	CpCp*ZrMe ₂	23	54	H(SiHPh) _{<i>n</i>} H	—	2340	8250	48
	Cp ₂ TiMe ₂	20	168	H(SiHPh) ₁₀ H ^a	88	—	—	110
	Cp ₂ TiPh ₂	110	24	H(SiHPh) ₁₆₀ H ^b	83	730	960	49
	Cp ₂ TiPh ₂	110	24	H(SiHPh) ₃₀ H ^b	99	620	700	49
	Cp ₂ TiPh ₂	110	24	H(SiHPh) ₄₀ H ^{b, c}	40	620	780	49
	Cp ₂ Ti(OPh) ₂	20	24	H(SiHPh) _{<i>n</i>} H	25	—	2400	110
	Cp ₂ Ti(OC ₆ H ₄ OMe-4) ₂	20	48	H(SiHPh) _{<i>n</i>} H	25	—	3100	110
	Cp ₂ Ti(OC ₆ H ₄ Cl-4) ₂	25	72	H(SiHPh) _{<i>n</i>} H	30	—	2200	110
	Cp ₂ Ti(OC ₆ H ₄ CN-4) ₂	25	72	H(SiHPh) _{<i>n</i>} H	30	—	2200	110
	Cp ₂ Ti(OC ₆ H ₄ Me-4) ₂	25	72	H(SiHPh) _{<i>n</i>} H	30	—	2300	110
	Cp ₂ TiMe ₂	20	15	H(SiHPh) _{<i>n</i>} H	25	—	2700	110
	Cp ₂ Zr(OPh) ₂	20	72	H(SiHPh) _{<i>n</i>} H	10	—	3200	110
	CpCp*Zr[Si(SiMe ₃) ₃]Me	23	0.4	H(SiHPh) _{<i>n</i>} H	—	1720	4750	48
	CpCp*Zr[Si(SiMe ₃) ₃]Me	23	24	H(SiHPh) _{<i>n</i>} H	—	1990	7660	48
	CpCp*Zr[Si(SiMe ₃) ₃]Me	23	48	H(SiHPh) _{<i>n</i>} H	—	2240	10 150	48
	Cp*(C ₅ H ₄ Me)Zr[Si(SiMe ₃) ₃]Me	23	48	H(SiHPh) _{<i>n</i>} H	—	1560	6110	48
	(η ⁵ -C ₅ H ₄ SiMe ₃) ₂ ZrMe ₂	23	24	H(SiHPh) _{<i>n</i>} H	—	1270	3080	48
	Cp*(η ⁵ -C ₆ H ₄ SiMe ₃)ZrH ₂	23	14	H(SiHPh) _{<i>n</i>} H	—	1660	8630	48
	CpSiMe ₂ CpZr[Si(SiMe ₃) ₃]Me	23	24	H(SiHPh) _{<i>n</i>} H	—	1910	5090	48
	CpSiMe ₂ CpZr[Si(SiMe ₃) ₃]Me	23	48	H(SiHPh) _{<i>n</i>} H	—	1730	5250	48
	CpSiMe ₂ CpZrMe ₂	23	3	H(SiHPh) _{<i>n</i>} H	—	1880	3770	48
	CpSiMe ₂ CpZrMe ₂	23	48	H(SiHPh) _{<i>n</i>} H	—	1570	3890	48
	Cp ₂ V	100–120	40	H(SiHPh) ₂ H,	40			82
				H(SiHPh) ₃ H	20			
	Cp ₂ VMe ₂	100–120	40	H(SiHPh) ₂ H,	40			82
				H(SiHPh) ₃ H	20			
Ph ₂ SiH ₂	Cp ₂ TiMe ₂	25	29	[Ph ₂ SiH] ₄	100			111
9,10-Dihydro-9-sila-anthracene (5a)	Cp ₂ ZrMe ₂	90	10	dimer,	12			111
				trimer	87			
10,11-Dihydro-5 <i>H</i> -di-benzo[<i>b,f</i>]silepine (5b)	Cp ₂ ZrMe ₂	105	72	dimer	20 ^d			111
Ph ₂ SiH ₂	Cp ₂ TiPh ₂	110	24	[Ph ₂ SiH] ₂	72			49
	Cp ₂ TiPh ₂	110	24	[Ph ₂ SiH] ₂	66 ^e			49
	Cp ₂ TiPh ₂	110	24	[Ph ₂ SiH] ₂	72 ^c			49
	Cp ₂ Ti(OPh) ₂	80	5	[Ph ₂ SiH] ₂	10			110
MePhSiH ₂	Cp ₂ TiPh ₂	110	24	(MePhSiH) ₂ ,	14			49
				H(MePhSi) ₃ H	32			
	Cp ₂ TiPh ₂	110	24	(MePhSiH) ₂ ,	15 ^e			49
				H(MePhSi) ₃ H	23 ^c			
	Cp ₂ TiPh ₂	110	24	(MePhSiH) ₂ ,	7			49
				H(MePhSi) ₃ H	88			

^a In the presence of a hydrogen acceptor; ^b the highest degree of polymerisation; ^c in the presence of cyclooctene; ^d 52% of unidentified oligomers; ^e in the presence of dec-1-ene.

The reactivity of RSiH₃ upon catalysis by dimethyltitanocene decreases in the following series (the relative reaction rates at 20 °C are given in parentheses): Ph (13) > Bn (1) = C₆H₁₃ (1). In the reactions catalysed by dimethylzirconocene, the reactivity changes in the following order: Ph (100) > Bn (15) > C₆H₁₃ (5).⁹¹

Zirconocenes catalyse dehydrocondensation of substituted phenylsilanes XC₆H₄SiH₃ containing the fluoroalkyl, alkoxy, aryloxy, acyloxy, hydroxy or alkylamino groups in the benzene

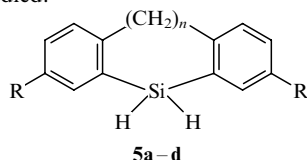
ring.¹¹⁰ Thus a polymer with the molecular weight of 1330 was prepared from 4-(dimethylamino)phenylsilane.¹¹⁰

The only convenient procedure for the synthesis of polymethylsilane involves dehydrocondensation of methylsilane catalysed by dimethyltitanocene or dimethylzirconocene at 50 °C and 10 atm.⁹² The molecular weight of the resulting cross-linked polymethylsilane is rather high (~ 10 000).

Disubstituted silanes, such as MeSiH₂Ph and Ph₂SiH₂, are less reactive than RSiH₃. In the presence of dimethyltitanocene or

dimethylzirconocene at 60–80 °C, these silanes form predominantly dimers and trimers, *viz.*, $\text{RH}_2\text{SiSiH}_2\text{R}$ and $(\text{R}_2\text{SiH})_2\cdot\text{SiHR}$.^{91,92} The catalytic activity of metallocenes Cp_2MMe_2 in this reaction decreases in the series $\text{Zr} > \text{Ti} \gg \text{Hf}$.^{89,91,92} When zirconocene, which was prepared *in situ* by the reaction of Cp_2ZrCl_2 with BuLi, was used as a catalyst, methylphenylsilane was converted into the linear $\text{H}(\text{MePhSi})_n\text{H}$ oligomer, where $n = 5$ or 6.¹¹³ Unlike methylphenylsilane, butylmethylsilane^{91,92} as well as other silanes R_3SiH (see Ref. 42) remained unchanged in the presence of dimethyltitanocene or dimethylzirconocene even at 100 °C.

Dehydrocondensation of dibenzosilaheterocycles **5a–d** was studied.¹¹²



R = H: $n = 1$ (**a**), 2 (**b**), 0 (**c**);
R = Bu^t, $n = 0$ (**d**).

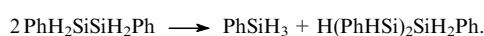
Dehydrocondensation of 9,10-dihydro-9-silaanthracene **5a** in the presence of dimethyltitanocene at 20 °C does not occur. In the reaction catalysed by dimethylzirconocene at 90 °C, the corresponding trimer is formed in high yield. Under analogous conditions in the presence of the same catalysts, 10,11-dihydro-5H-dibenzo[*b,f*]silepine (**5b**) remains unchanged. Silafluorene (**5c**) is converted into a pentamer, which is insoluble in the usual organic solvents, upon catalysis by dimethyltitanocene in toluene in the absence of oxygen for 29 h.

Titanium and zirconium complexes with the [2-(diisopropylamino)ethyl]cyclopentadienyl ligand, *viz.*, $[\text{Cp}(\text{CH}_2)_2\text{NPr}_2]_2\text{MMe}_2$ ($\text{M} = \text{Ti}$ or Zr), $[\text{Cp}(\text{CH}_2)_2\text{NPr}_2]_2\text{TiBr}_2$ and $[\text{Cp}(\text{CH}_2)_2\cdot\text{NPr}_2]_2\text{Ti}(\text{OPh})_2$, were suggested as efficient catalysts of dehydrocondensation of phenylsilane.¹¹⁴

Binary mixtures of dimethyltitanocene with one equivalent of trialkyl- or alkylarylphosphine are used as catalysts of dehydrocondensation of PhSiH_3 , MePhSiH_2 , Ph_2SiH_2 and BnSiH_3 .^{97–99} In these cases, microcrystalline products are formed.

Nakano and coworkers⁴⁹ succeeded in performing dehydrocondensation of triphenyl-, diphenyl- and methylphenylsilanes in the presence of Cp_2TiPh_2 (under an argon atmosphere, 110 °C, 24 h). In this case, 1,1,2,2-tetraphenyldisilane (72%) formed from diphenylsilane, whereas 1,2,3-trimethyl-1,2,3-triphenyltrisilane (32%) and 1,2-dimethyl-1,2-diphenyldisilane (14%) were obtained from methylphenylsilane. When cyclooctene was used as an acceptor of hydrogen, which was eliminated upon dehydrocondensation, the yield of trisilane was increased to 80%. Dehydrocondensation of phenylsilane under analogous conditions proceeds more readily to yield polyphenylsilanes containing terminal hydrogen atoms ($M = 340–17\,300$). The reaction of phenylsilane in the presence of Cp_2TiPh_2 at 140 °C for 3 h afforded a cyclic six-membered silane.¹¹⁵ Under analogous conditions, triethylsilane generates hexaethyldisilane in insignificant yield (0.6%).

Dehydrocondensation of 1,2-diphenyldisilane catalysed by dimethyltitanocene or dimethylzirconocene proceeds very rapidly. Thus the $\text{H}(\text{PhSiH})_4$ tetramer was obtained in 40% yield after 30 min.⁹¹ Apparently, the presence of PhSiH_3 and $\text{H}(\text{PhHSi})_2\cdot\text{SiH}_2\text{Ph}$ among the reaction products results from competitive disproportionation of the initial 1,2-diphenyldisilane



The enhanced reactivity of 1,2-diphenyldisilane is determined by the lower energy of the Si–H bonds in the $-\text{H}_2\text{Si}-\text{SiH}_2-$ fragment compared to their energy in the SiH_3 group.

Dehydrocondensation of silanes of the $\text{Si}_a\text{H}_b\text{R}_c$ type [$\text{R} = \text{Alk}$, Ar , alkenyl, AlkO , Hal or NR_2 ; $a \geq 2$; $b \geq 1$; $(b + c) = (2a + 2)$] catalysed by dialkylmetallocenes Cp_2MAlk_2 ($\text{M} = \text{Ti}$, Zr or Hf) afforded liquid linear polymers containing from three to seven monomer units.^{83–85}

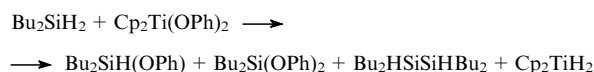
Dehydrocondensation of phenylsilane with 1,2-dimethyldisilane in the presence of Cp_2MMe_2 ($\text{M} = \text{Ti}$ or Zr) yielded the $\text{H}[(\text{MeSiH})_x(\text{PhSiH})_y]_n\text{H}$ oligomer.¹¹⁶

The reaction of $\text{Me}_2\text{HSiSiH}_2\text{Me}$ with 1,2-dimethyldisilane afforded the $\text{H}[(\text{MeSi})_x(\text{Me}_2\text{Si})_y]_n\text{H}$ oligomer. The structures of these oligomers were established by GLC-mass spectrometry.¹¹⁶

b. Catalysis by alkoxy- and aryloxymetallocenes and titanium alkoxides

Dehydrocondensation of phenyl-, diphenyl- and dibutylsilane catalysed by dialkoxy-, diphenoxytitanocene, its derivatives $\text{Cp}_2\text{Ti}(\text{OR})_2$ ($\text{R} = \text{Alk}$, Ph , 4- MeC_6H_4 , 4- MeOC_6H_4 , 4- ClC_6H_4 or 4- CNC_6H_4) or diphenoxyzirconocene $\text{Cp}_2\text{Zr}(\text{OPh})_2$ was studied.^{117–120} Dehydrocondensation of PhSiH_3 afforded a mixture of linear and cyclic oligomers (15 min, 50 °C, the total yield was 25%). In this case, the reaction rate and the compositions of the resulting oligomers are comparable with those observed in the reactions with the use of Cp_2TiMe_2 (see Ref. 87) or the $\text{Cp}_2\text{TiCl}_2-2\text{BuLi}$ binary mixture¹¹³ as catalysts.

In the presence of $\text{Cp}_2\text{Ti}(\text{OPh})_2$ at 100 °C, diphenylsilane formed the $\text{Ph}_2\text{SiHSiHPh}_2$ dimer in 10% yield.¹¹¹ In the presence of 5 mol. % of $\text{Cp}_2\text{Ti}(\text{OPh})_2$ at 110 °C, dibutylsilane gave mono- and diphenoxy derivatives due to the interaction with the catalyst.

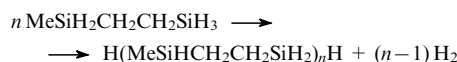


For the reaction to start, preliminary heating of the reaction mixture is required. In this case, an induction period from 15 to 120 min was observed. Probably, the reduction of the Ti–OPh bonds in the catalyst to form an intermediate hydride complex occurs in one of the initial stages.¹¹⁹ Diphenoxytitanocene derivatives containing substituents in the benzene ring, *viz.*, $\text{Cp}_2\text{Ti}(\text{OC}_6\text{H}_4\text{X}-4)_2$ ($\text{X} = \text{Me}$, Cl , CN or OMe), exhibit higher catalytic activity. In the presence of these complexes even at 20 °C, phenylsilane yielded products identical to those obtained at 50 °C in the presence of diphenoxytitanocene (see Table 1).¹¹⁹

Dehydrocondensation of diphenylsilane catalysed by diphenoxyzirconocene occurs at 20 °C with elimination of hydrogen. However, an induction period was also observed and prior heating (50 °C, 15 min) of the reaction mixture is required. In this case, the amount of cyclic oligomers among the reaction products is smaller than that obtained with the use of diphenoxytitanocene.¹¹⁹

Dehydrocondensation of phenylsilane in the presence of dicyclopentadienylzirconium dimethoxide as a catalyst was reported.¹²¹

Dehydrocondensation of 1,4-disilapentane catalysed by diphenoxytitanocene was described.¹¹⁹ The rate of this reaction is smaller than that in the case of phenylsilane and is close to that observed with the use of dimethyltitanocene or the $\text{Cp}_2\text{TiCl}_2-2\text{BuLi}$ system as catalysts.¹²² Initially, the catalyst was activated at 0 °C and then the reaction was performed at 20 °C. In this case, exclusively SiH_3 groups reacted resulting in a linear oligomer containing the SiMeH_2 fragments. This oligomer was converted into an insoluble cross-linked polymer upon heating.¹¹⁹



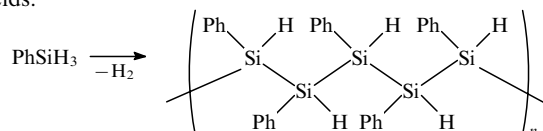
Alkoxy derivatives of titanium, which do not contain cyclopentadienyl ligands, such as $\text{Ti}(\text{OPr}^i)_4$ or $\text{MeTi}(\text{OPr}^i)_3$, were also used as catalysts of dehydrocondensation of alkyl- and arylsilanes.¹¹⁷

c. Catalysis by metallocene chlorides and the $\text{Cp}_2\text{MHal}_2-\text{RLi}(\text{RMgX})$ systems

Metallocene dichlorides Cp_2MCl_2 are similar to Cp_2MMe_2 ($\text{M} = \text{Ti}$ or Zr) in catalytic activity.^{90,123} The activity of Cp_2HfCl_2 is substantially lower than that of Cp_2HfMe_2 , but it can be enhanced by adding MeLi in a molecular ratio of 1:2. In this case, both chlorine atoms are apparently completely replaced by

the methyl groups. Dehydrocondensation of phenylsilane in the presence of a mixture of Cp_2HfCl_2 and MeLi afforded cyclophenylsilanes in 15% yield.⁹⁰ When the reagents were taken in a ratio of 1:3 or 1:4, the yield of $(\text{PhSiH})_n$ was only 25%; the molecular weights of the resulting phenylcyclodisilanes were larger than those obtained with the use of dimethyltitanocene or dimethylzirconocene as a catalyst.⁹⁰ When a mixture of [1,2-bis(tetrahydroindenyl)ethane]dichlorozirconium with MeLi taken in a ratio of 1:2 was used, cyclophenylsilanes were formed in 42% yield.¹²³

Dehydrocondensation of phenylsilane catalysed by zirconocene derivatives of the $\text{Cp}_2\text{ZrX(Y)}$ type ($\text{X} = \text{H}$ or Cl and $\text{Y} = \text{Cl}$ or Alk) yields stereoregular polyphenylsilane in good yields.^{124–126}



It was expected⁹⁰ that dehydrocondensation of phenylsilane catalysed by Zr complexes containing ethylenebis(tetrahydroindenyl) or -indenyl ligands would also afford stereoregular polyphenylsilanes, unlike the reactions catalysed by biscyclopentadienyl complexes of Ti and Zr, which yield atactic polymers. According to the data of ^1H NMR spectroscopy and gel-permeation chromatography, this reaction afforded a mixture of linear and cyclic oligomers, which hindered the interpretation of the microstructure of the resulting polymer. It should be remembered that, for example, nine stereoisomers of hexaphenylcyclohexasilane possessing 23 chiral centres can exist.⁹⁰

Dehydrocondensation of hydrosilanes RSiH_3 ($\text{R} = \text{Bu}^n$, C_6H_{13} or Ph) catalysed by the $\text{Cp}_2\text{MCl}_2-2\text{BuLi}$ system ($\text{M} = \text{Ti}$, Zr or Hf) was studied in detail.^{127–130} The course of the reaction was monitored by gas chromatography and GLC-mass spectrometry. Dehydrocondensation of phenylsilane afforded linear oligomers with $M = 1775$ and 614 ($M_w:M_n = 1.17$ and 1.01 , respectively, when Cp_2ZrCl_2 was used) and $M = 1308$ and 600 ($M_w:M_n = 1.09$ and 1.03 , respectively, when Cp_2TiCl_2 was used). Therefore, the molecular weight of the dehydrocondensation products of phenylsilane is affected by the nature of the catalyst. The molecular weight increases in the series $\text{Hf} \ll \text{Ti} \ll \text{Zr}$, as in the case of the use of individual metallocenes.⁸² Dehydrocondensation of diphenylsilane catalysed by the $\text{Cp}_2\text{HfCl}_2-2\text{BuLi}$ system at 20°C for 1 h yielded only 1,1,2,2-tetraphenyldisilane. When the temperature was increased to 50°C , higher oligomers up to decaphenylpentasilane (the yield was 17%) were also obtained after 5 h. Under analogous conditions, butylsilane in the presence of the $\text{Cp}_2\text{MCl}_2-2\text{BuLi}$ system ($\text{M} = \text{Ti}$ or Zr) was converted into a mixture of linear and cyclic oligomers containing up to 11 silicon atoms. Two individual diastereomers of tetrabutyltetrasilane were isolated from this mixture. It is remarkable that the ratio of the diastereomers remained unchanged in the course of the reaction if $\text{M} = \text{Ti}$, whereas in the case of $\text{M} = \text{Zr}$, the diastereomers were formed at different rates.

Hexylsilane in the presence of the $\text{Cp}_2\text{ZrCl}_2-2\text{BuLi}$ system forms linear and cyclic tetra- and heptamers.¹²⁷

Dehydrocondensation of $\text{R}^1\text{R}^2\text{SiH}_2$ ($\text{R}^1 = \text{Ph}$ and $\text{R}^2 = \text{Me}$; $\text{R}^1 = \text{R}^2 = \text{Ph}$; or $\text{R}^1 = 3\text{-MeC}_6\text{H}_4$ and $\text{R}^2 = \text{Me}$) and dibenzosilaheterocycles **5a,b,d** in the presence of the $\text{Cp}_2\text{MCl}_2-2\text{BuLi}$ system ($\text{M} = \text{Ti}$, Zr or Hf) was studied.¹¹³ In the case of dehydrocondensation of MePhSiH_2 (90°C , 24 h), the activity of these catalysts increases in the series $\text{Hf} < \text{Ti} < \text{Zr}$. Linear oligomers containing from 2 to 8 silicon atoms are the major reaction products. At $20\text{--}90^\circ\text{C}$, more sterically hindered diphenylsilane yields only tetraphenyldisilane. Silafluorene (**5d**) reacted analogously to give (after 2 h) the corresponding disilane in 82% yield. Dehydrocondensation of 9,10-dihydro-9-silaanthracene (**5a**) in the presence of the binary catalyst proceeds substantially more slowly than the reaction with the use of dimethyltitanocene.

Dibenzosilolepine (**5b**) remained unchanged at 90°C in the presence of any catalytic system based on zirconium. The use of ethyl-, isopropyl- or butylmagnesium chlorides instead of BuLi (90°C , 24 h, toluene) led to a substantial decrease in the proportion of tri- and tetramers. The binary $\text{Cp}_2\text{ZrCl}_2-\text{BuLi}$ system is an efficient catalyst of dehydrocondensation of diorganylsilanes, but its use, unlike dimethyltitanocene, leads predominantly to the formation of short-chain oligomers.¹¹³

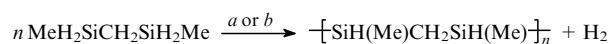
Syndiotactic polyphenylsilanes with high M_w ($> 10\,000$) were prepared by dehydrocondensation of phenylsilane in the presence of a mixture of the zirconium complex $\{\text{Cp}^*[\text{Cp}(\text{CH}_2)_n\text{NMe}_2]\text{ZrCl}_2$ ($n = 2$ or 3) or $\text{Cp}^*[\text{Cp}(\text{CH}_2)_n\text{CHMe}_2]\text{ZrCl}_2$ ($n = 1$ or 2) with two equivalents of BuLi .^{131,132}

The catalytic activity of pure dimethyltitanocene as well as of its mixture with butyllithium decreases substantially in the presence of atmospheric oxygen.¹²²

Dehydrocondensation of silanes [both symmetrical, *viz.*, $\text{H}(\text{PhMeSi})_2\text{H}$ and $\text{H}(\text{BuMeSi})_2\text{H}$, and unsymmetrical, *viz.*, $\text{HPh}_2\text{SiSiPhMeH}$, $\text{HPhMeSiSiMe}_2\text{H}$, HPhMeSiSiPrMeH and $\text{HPh}_2\text{SiSiPhH}_2$] catalysed by the $\text{Cp}_2\text{MCl}_2-2\text{BuLi}$ system ($\text{M} = \text{Ti}$ or Zr) in the presence of cyclooctene was studied.^{133,134} When the disilane:cyclooctene: Cp_2MCl_2 ratio was $30:(>30):1$, trisilanes were rapidly formed from $\text{HPh}_2\text{SiSiPhMeH}$ and $\text{HPhMeSiSiMe}_2\text{H}$. The products were identified by GLC-mass spectrometry. Dehydrocondensation of $\text{HPh}_2\text{SiSiPhH}_2$ afforded Ph_2SiH_2 and PhSiH_3 , which were subsequently converted into a mixture of linear and cyclic polysilanes. These data indicate that dehydrocondensation is accompanied by the cleavage of the Si–Si bond in the initial disilane.

Dehydrocondensation of RSiH_3 and $\text{RH}_2\text{SiSiH}_2\text{R}$, where the R substituent is the $\text{Cp}(\text{CO})_2\text{Fe}$ metallocene group, was performed in the presence of the $\text{Cp}_2\text{MCl}_2-\text{BuLi}$ system ($\text{M} = \text{Ti}$ or Zr). Dehydrocondensation of $\text{Cp}(\text{CO})_2\text{FeSiH}_3$ and $\text{Cp}(\text{CO})_2\text{FeSiH}_2\text{SiH}_2\text{Fe}(\text{CO})_2\text{Cp}$ gave organometallic oligosilanes characterised by spectroscopic and chromatographic methods.¹³⁵

Dehydrocondensation of 2,4-disilapentane catalysed by the $\text{Cp}_2\text{ZrCl}_2-2\text{BuLi}$ or $\text{Cp}_2\text{TiCl}_2-2\text{MeLi}$ system afforded new poly(silacarbo)silanes containing the SiCH_2Si fragments in the main chain.^{43,128}

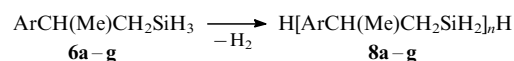


(a) $\text{Cp}_2\text{ZrCl}_2-2\text{BuLi}$; (b) $\text{Cp}_2\text{TiCl}_2-2\text{MeLi}$.

This reaction yielded predominantly oligomers (50%–80%), while di- and trimeric products were formed in insignificant amounts. The yields of oligomers depend substantially on the nature of the metal atom in the metallocene, the duration of the reaction and the concentration of the monomer. The $\text{Cp}_2\text{ZrCl}_2-2\text{BuLi}$ catalytic system is more efficient than the $\text{Cp}_2\text{TiCl}_2-2\text{MeLi}$ system (the yields of oligomers are 80% and 50%, respectively). The degree of condensation of these monomers is somewhat higher than that of PhMeSiH_2 ; the resulting polymers are characterised by moderate M values, which indicates that they are partially cross-linked.^{86,89,113} The higher reactivity of 2,4-disilapentane compared to phenylmethylsilane is attributable to the favourable steric factors.

d. Catalysis by the $\text{Cp}_2\text{MCl}_2-\text{Al}$ system

Dehydrocondensation of 3-arylpropylsilanes **6a–g** as well as of 2-phenyl-1,3-disilapropane [$\text{H}_3\text{SiCH}_2\text{CH}(\text{Ph})\text{CH}_2\text{SiH}_3$, **7**] catalysed by the $\text{Cp}_2\text{MCl}_2-\text{Al}$ system ($\text{M} = \text{Ti}$ or Hf) was performed.^{44,45}



$\text{Ar} = \text{Ph}$ (**a**), 4- MeC_6H_4 (**b**), 2,5- $\text{Me}_2\text{C}_6\text{H}_3$ (**c**), ClC_6H_4 (**d**, mixture of isomers), 4- $\text{MeC}_6\text{H}_3\text{Cl}$ (**e**, mixture of isomers), PhOC_6H_4 (**f**, mixture of isomers), C_{10}H_7 (**g**, mixture of isomers).

Substituted polysilanes **8a–g** prepared from compounds **6a–g** have predominantly linear structures and molecular weights from 800 to 1028 (the degree of polymerisation is 3–7, $M = \text{Hf}$) and from 800 to 1300 (the degree of polymerisation is 6–16, $M = \text{Ti}$), *i.e.*, the molecular weights are higher than those of the analogous polyarylsilanes synthesised in the presence of other catalytic systems.^{42,46} The catalytic activity of the $\text{Cp}_2\text{HfCl}_2\text{–Al}$ system is lower than that of its titanium analogue (the yields of polysilanes are 31%–84% and 79%–99%, respectively).

The reaction rate increases both as the concentration of the catalyst increases [from 0.5 mol. % to 10 mol. % ($M = \text{Ti}$) or from 1.0 mol. % to 6.5 mol. % ($M = \text{Hf}$)] and as the reaction temperature increases to 90 °C. Dehydrocondensation of compound **7** catalysed by the $\text{Cp}_2\text{TiCl}_2\text{–Al}$ system proceeded smoothly and the total yield of polysilanes reached 90%.⁴⁴ Two polymeric reaction products were isolated from the resulting mixture by column chromatography. One of these products is a viscous weakly cross-linked soluble polysilane ($M_w = 1046$, $M_n = 819$, $n = 11$) and the second product is a completely cross-linked insoluble white solid polymer.

Dehydrocondensation of organylsilanes **6b** and **6d**, **6b** and **6f** or **6d** and **6f** catalysed by the $\text{Cp}_2\text{TiCl}_2\text{–Al}$ system afforded the corresponding cooligomers (the yields were 51%–86%) with $M_w = 678\text{–}994$ and $M_n = 405\text{–}538$ (the degree of copolymerisation was 7).⁴⁴

e. Catalysis by the ternary $\text{Cp}_2\text{MCl}_2\text{–RLi–B}(\text{C}_6\text{F}_5)_3$ system and by the cationic bis(cyclopentadienyl) complexes of zirconium and hafnium

Dehydrocondensation of phenylsilanes in the presence of the ternary Cp_2MCl_2 ($\text{CpCp}^*\text{MCl}_2$)–2 BuLi– $\text{B}(\text{C}_6\text{F}_5)_3$ catalytic system ($M = \text{Ti}$, Zr or Hf) afforded polyphenylsilanes with $M = 10\,910\text{–}13\,790$.^{47,95,96} It is remarkable that when the reaction was performed in the presence of only $\text{B}(\text{C}_6\text{F}_5)_3$ at 20 °C for 10 days, the molecular weight of the resulting polyphenylsilane reached only 2450. In both cases, the ratio between linear and cyclic polymers remained the same.⁴⁷ The addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to the $\text{Cp}_2\text{MCl}_2\text{–BuLi}$ catalytic system changes the ratio between the cyclic and linear dehydrocondensation products from 45:55 to 15:85. The catalytic activity of zirconocenes both in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ and in its absence increases in the series $\text{Cp}_2^*\text{Zr} \ll \text{Cp}_2\text{Zr} \approx (\text{MeC}_5\text{H}_4)_2\text{Zr} < \text{CpCp}^*\text{Zr}$ (*cf.* Ref. 136). The $\text{Cp}_2\text{TiMe}_2\text{–B}(\text{C}_6\text{F}_5)_3$ and $[\text{Cp}_2\text{ZrMe}(\text{THF})](\text{BPh}_4)$ systems, which are successfully used for the polymerisation of alkenes,¹³⁷ do not catalyse dehydrocondensation of phenylsilane.⁴⁷

Dehydrocondensation of organylsilanes in the presence of the ternary catalytic system, which contains Group IVB metallocene, a trimethylsilyl derivative of alkali metal and THF, has been described.¹³⁸ Thus a polymer with $M = 6800$ was prepared from phenylsilane in the presence of the $\text{Cp}_2\text{HfCl}_2\text{–Me}_3\text{SiLi–THF}$ system.

Dehydrocondensation of phenylsilane in the presence of cationic bis(cyclopentadienyl) complexes of Zr and Hf was studied. These complexes were prepared *in situ* by the reactions of Cp_2MMe_2 ($M = \text{Zr}$ or Hf) with $[\text{Bu}_3\text{NH}]^+[\text{B}(\text{3,5-Me}_2\text{C}_6\text{H}_3)_4]^-$ or $[\text{PhMe}_2\text{NH}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$.⁴⁸ The activity of these catalysts appeared to be low. The total yield of cyclophenylsilanes at 23 °C is no higher than 13%. Dehydrocondensation with the use of the $\text{CpCp}^*\text{ZrMe}_2\text{–}[\text{Bu}_3\text{NH}]^+[\text{B}(\text{3,5-Me}_2\text{C}_6\text{H}_3)_4]^-$ system as a catalyst (23 °C, 1 h) affords linear and cyclic polyphenylsilanes with rather low M values (up to 2810). In this case, variations in the anion and the metal atom in the metallocene (Zr or Hf) have no substantial effect on the course of the process.⁴⁸

f. Catalysis by metallocenes containing organosilicon groups at the metal atom

Metallocenes (Ti, Zr or Hf) containing organosilicon groups at the metal atom were also suggested as catalysts of dehydrocon-

densation of organosilanes. In the presence of these catalysts, di- and trisubstituted silanes form linear (at ≤ 60 °C) or cyclic (at ≥ 80 °C) polysilanes.^{48,65,91,94,100,139–147} For example, dehydrocondensation of phenylsilane catalysed by $\text{Cp}_2\text{Ti}(\text{CH}_2\text{SiMe}_3)_2$ afforded linear polysilane (92%, $M = 1890$) and cyclic oligophenylsilane (95%, $M = 738$) at 30 °C (24 h) and 80 °C, respectively.¹³⁹

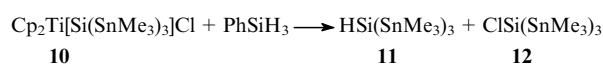
Dehydrocondensation of arylsilanes $\text{RC}_6\text{H}_4\text{SiH}_3$ ($R = \text{H}$, 4-Me, 3-Me, 2-Me, 4- CF_3 , 3- CF_3 or 2- CF_3) in the presence of $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$ yielded poly(trifluoromethylphenyl)-, poly(methylphenyl)silanes and polyphenylsilane.⁶⁵ In the dehydrocondensation process, the reactivity of $\text{RC}_6\text{H}_4\text{SiH}_3$ decreases depending on the radical R in the series (the relative reaction rates are given in parentheses) 4- CF_3 (1.34) $\approx$ 3- CF_3 (1.33) $>$ H (1.00) $>$ 4-Me (0.95) $\approx$ 3-Me (0.93) $\gg$ 2-Me (0.18) $\approx$ 2- CF_3 (0.14). These data indicate that the reaction rate is influenced both by the electronic and steric effects of the substituents in the aromatic core. 2-Substituted phenylsilanes exhibit the lowest activities. The molecular weights of poly(trifluoromethylphenyl)silanes and polyphenylsilanes obtained under analogous conditions are much the same.

Silyl complexes of zirconocene and hafnocene of the $\text{CpCp}'\text{M}(\text{SiR}^1)_3\text{R}^2$ type ($\text{Cp}' = \text{Cp}$ or Cp^* ; $M = \text{Zr}$ or Hf ; $\text{R}^1 = \text{Me}$, Ph or SiMe_3 ; $\text{R}^2 = \text{Alk}$, SiMe_3 or Cl) are also efficient catalysts of dehydrocondensation of arylsilanes. In these cases, the molecular weights of linear and cyclic polymers vary over wide ranges depending on the nature of the catalyst and the reaction conditions.^{48,140–142}

Phenylsilane in the presence of $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$ or $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ formed polymers with $M = 990$ and polymers with $M = 1240$ containing from 10 to 20 SiHPh monomer units after 15 min and 7 h, respectively. Phenylcyclasilane (containing from 5 to 8 silicon atoms) was identified among these polymers.^{14,48} It should be noted that polyphenylsilane with $M_n = 560$ was obtained upon catalysis by dimethylzirconocene during 24 h. Zirconocenes with mixed cyclopentadienyl ligands (nonsubstituted or partially or completely methylated) appeared to be more active catalysts in these reactions. The molecular weight of the linear polymer $\text{H}(\text{PhHSi})_n\text{H}$ formed in the presence of $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$ reached 3000 and 5260 after 15 min and 48 h, respectively. Linear and cyclic polymers contain about 70 silicon atoms in the polysilane chains (see Table 1).⁴⁸

Dehydrocondensation of methylphenyl- and diphenylsilanes catalysed by alkyne zirconocene and titanocene complexes of the $\text{Cp}_2\text{M}(\text{L})(\text{RC}\equiv\text{CSiMe}_3)$ type ($M = \text{Ti}$ or Zr ; $\text{L} = \text{THF}$ or Py) affords oligomers. Under these conditions, phenylsilane forms polymers.^{148,149}

The catalytic activities of the zirconium and titanium complexes, *viz.*, $(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ (**9**) and $\text{Cp}_2\text{Ti}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ (**10**), respectively, in dehydrocondensation of phenylsilane and dibutylstannane were studied.¹⁴³ According to the data of GLC-mass spectrometry, a viscous mixture of linear $\text{H}(\text{PhHSi})_n\text{H}$ and cyclic $(\text{PhSiH})_n$ ($n = 5$ or 6) oligomers ($M_n = 900$, $M_w = 1810$) was formed from phenylsilane in the presence of the complex **9** after 24 h. Under analogous conditions, a mixture of linear and cyclic polysilanes with $M_n = 1870$ and $M_w = 3280$ was formed upon catalysis by the $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ complex, which does not contain the trimethylsilyl group in the cyclopentadienyl ring. Dehydrocondensation of dibutylstannane in the presence of the complex **9** affords polybutylstannanes with a broad molecular weight distribution spectrum ($M_w = 4800$, $M_n = 1420$). The reaction of the complex **10** with an equivalent amount of phenylsilane in C_6D_6 gave a mixture of the metathesis product **11** and the reductive elimination product **12** in a ratio of 2:1 in quantitative yield.¹⁴³



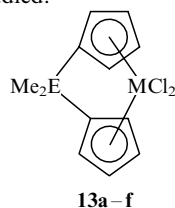
Dehydrocondensation of 1,4- $\text{RH}_2\text{SiC}_6\text{H}_4\text{SiH}_2\text{R}$ ($R = \text{Me}$, Et or C_6H_{13}) catalysed by $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$ under mild

conditions (20 °C) afforded linear oligomers $\text{RH}_2\text{Si}(\text{C}_6\text{H}_4\text{SiHR})_n\text{C}_6\text{H}_4\text{SiHR}$. Further heating of the resulting mixture of oligomers ($\text{R} = \text{Me}$ or Et) led to an increase in the molecular weight due to partial cross-linking of the polymer chains through free Si–H groups. Thermolysis of the insoluble cross-linked polymer $\text{EtH}_2\text{Si}(\text{C}_6\text{H}_4\text{SiHEtSiHEt})_n\text{C}_6\text{H}_4\text{SiH}_2\text{Et}$ at 1100 °C afforded ceramics in higher yield (67%) than that with the use of the corresponding low-molecular-weight oligomers (35%).¹⁵⁰

It was reported that the $\text{Cp}_2\text{Zr}(\text{OMe})_2 - (\text{Me}_3\text{Si})_3\text{SiLi} - 3 \text{ THF}$ ternary system was used as a catalyst of dehydrocondensation of phenylsilane.¹²¹

g. Catalysis by ansa-metalloenes

Dehydrocondensation of phenyl- and methylphenylsilane catalysed by ansa-metalloenes (**13a–f**),^{144, 145, 151, 152} which are used for the preparation of iso- and syndiotactic polypropylenes, was studied.^{153, 154}



$\text{E} = \text{Si}; \text{M} = \text{Ti} \text{ (a)}, \text{Zr} \text{ (b)}, \text{Hf} \text{ (c)}$
 $\text{E} = \text{C}; \text{M} = \text{Ti} \text{ (d)}, \text{Zr} \text{ (e)}, \text{Hf} \text{ (f)}$

Methylphenylsilane in the presence of ansa-metalloenes with a BuLi cocatalyst (the ratio is 22 : 1 : 2) in toluene at 90 °C formed low-molecular-weight oligomers, viz., the corresponding di-, tri- and tetrasilanes. In this case, tetramers existed in the reaction mixture in insignificant amounts (1.8%–5.5% according to the GLC data). In the presence of ansa-hafnocene, tetrasilane is not formed at all. The activity of ansa-metalloenes, which was estimated from the yield of disilane after 24 h, decreases in the series $\text{Ti} > \text{Hf} > \text{Zr}$.

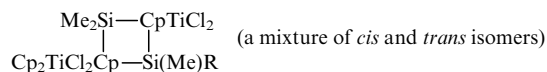
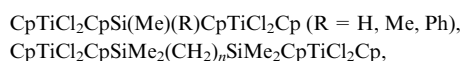
Catalyst	13a	13c	13b	13d	13f	13e
Yield of disilane according to GLC (%)	36	30	22	58	37	25

The activity of metallocene dichlorides in dehydrocondensation of methylphenylsilane decreases in the series $\text{Hf} (37) > \text{Ti} (32) > \text{Zr} (15)$ (the yields of disilane according to the GLC data are given in parentheses). 1,2-Dimethyl-1,2-diphenyldisilane and 1,2,3-trimethyl-1,2,3-triphenyltrisilane prepared from methylphenylsilane exist as mixtures of diastereomers. Dehydrocondensation of phenylsilane catalysed by ansa-metalloenes (Ti , Zr or Hf) in the absence of a solvent affords a mixture of linear and cyclic polyphenylsilanes. In this case, the molecular weight of the linear polymer increases in the series $\text{Ti} < \text{Zr} < \text{Hf}$.¹⁴⁴ Under analogous conditions (the silane : complex : BuLi ratio is 24 : 1 : 2, 13–24 h, 20 °C), the molecular weight of polyphenylsilanes prepared in the absence of ansa-metalloenes is always lower than that obtained with the use of usual metallocenes.

e. Catalysis by binuclear titanium and zirconium complexes

Dehydrocondensation of phenyl-, benzyl-, hexyl- and diphenylsilanes catalysed by the binuclear titanium complexes $\text{Cp}_2\text{Ti}(\mu\text{-HSiHPh})_2\text{TiCp}_2$ and $\text{Cp}_2\text{Ti}(\mu\text{-H})(\mu\text{-HSiHPh})\text{TiCp}_2$ generally affords oligomers.¹⁰⁰ Alkenes, the activating action of which increases in the series cyclohexene < 2-pentene < 1-pentene ~ norbornene ~ styrene, are used as cocatalysts, which substantially enhance the rate of this reaction.

It was reported¹⁴⁶ that binuclear titanocene complexes can be used as catalysts of dehydrocondensation of phenylsilane, for example



These reactions give mixtures of linear and cyclic polyphenylsilanes;¹⁴⁶ BuLi is used as a cocatalyst.

3. Catalysis by compounds of Group VB–VIIB elements

The data on the use of compounds of Group VB–VIIB metals as catalysts of dehydrocondensation of organylsilanes are scarce. Vanadocene Cp_2V and dimethylvanadocene Cp_2VMe_2 do not catalyse this reaction at 20 °C.⁸² However, phenylsilane in boiling toluene in the presence of these compounds was converted into a mixture of the $\text{PhH}_2\text{SiSiH}_2\text{Ph}$ dimer (40%) and the $(\text{PhSiH}_2)_2\text{SiHPh}$ trimer (20%). Under analogous conditions (100–120 °C, 123 h), higher metallocenes Cp_2M ($\text{M} = \text{Nb}$ or Ta) do not catalyse dehydrocondensation of phenylsilane. Neither at high temperature (115–120 °C) nor upon UV irradiation is this reaction catalysed by hydride complexes of niobium or tantalum Cp_2MH_3 ($\text{M} = \text{Nb}$ or Ta),⁸² whereas phenylsilane actively undergoes dimerisation in the presence of trimethylsilyl derivatives of tantalocene $\text{Cp}^*\text{Ta}(\text{SiMe}_3)\text{Cl}_3$. In this case, reduction products of the catalyst, viz., trimethylsilane and the tantalum hydride complex $[\text{Cp}^*\text{TaHCl}_3]_n$, are formed along with 1,2-diphenyldisilane.⁴⁶

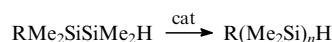
Cyclopentadienyl complexes of chromium, molybdenum and tungsten, viz., Cp_2Cr , Cp_2MoH_2 and Cp_2WH_2 , do not catalyse dehydrocondensation of PhSiH_3 at room temperature as well as under irradiation.⁸² Cyclopentadienyl chromium complexes, such as $(\eta^6\text{-H}_3\text{SiC}_6\text{H}_5)\text{Cr}(\text{CO})_3$, act as catalysts of dehydrocondensation of silanes. In this case, the corresponding polysilanes containing chromium carbonyls in the side chain are formed.¹⁵⁵

Some binary carbonyl complexes of manganese catalyse dehydrocondensation of phenylsilane at 100 °C.⁶⁸

4. Catalysis by compounds of Group VIIIB elements

The use of platinum complexes as catalysts of dehydrocondensation of pentamethyldisilane and symmetrical tetramethyldisilane was reported for the first time in 1970.¹⁵⁶ Later on, these reactions were described as disproportionations catalysed by phosphine complexes of platinum metals.¹⁵⁷

It was found that penta- and tetramethyldisilanes were converted into the $(\text{Me}_3\text{SiSiMe}_2)_2$ dimer or a mixture of $\text{H}(\text{Me}_2\text{SiSiMe}_2)_n\text{H}$ oligomers ($n = 2-6$), respectively, in the presence of platinum bis(triethylphosphine) dichloride at 90 °C (18 h).^{156–158}



$\text{R} = \text{H}, \text{Me}; n = 2-6; \text{cat} = \textit{trans}\text{-}[\text{PtCl}_2(\text{PEt}_3)_2], [\text{NiCl}_2(\text{PEt}_3)_2] \text{ etc.}$

The ethylenebisphosphine complex of platinum $[\text{C}_2\text{H}_4\text{Pt}(\text{PPh}_3)_2]$ at room temperature does not induce dehydrocondensation of silanes, such as Ph_3SiH , Me_2PhSiH , Et_3SiH and $(\text{EtO})_3\text{SiH}$.^{109, 112} However, MePhSiH_2 and Et_2SiH_2 in the presence of this complex were converted into the corresponding dimers in 27% and 95% yields, respectively.¹⁰⁹ It is remarkable that in the case of Et_2SiH_2 , dehydrocondensation occurs more readily than hydrosilylation of 1-hexene. In attempting to perform hydrosilylation of 1-hexene with a mixture of Et_3SiH and Et_2SiH_2 , only dehydrocondensation products $\text{Et}_2\text{HSiSiHEt}_2$ and $\text{Et}_2\text{HSiSiEt}_3$ were obtained in a ratio 7 : 1. In this case, hexaethyldisilane was not formed. The dehydrocondensation product, viz., tetraethyldisilane, was also not detected upon hydrosilylation of 1-hexene with diethyldisilane in the presence of H_2PtCl_6 (Spier's catalyst) or Ph_2PtCl_2 .¹⁰⁹

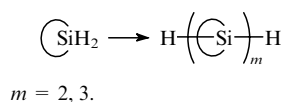
Dehydrocondensation of acyclic and cyclic disubstituted silanes $\text{R}^1\text{R}^2\text{SiH}_2$ [R^1 and $\text{R}^2 = \text{Alk}$, $(\text{CH}_2)_n$ ($n = 3-5$) or 1,2- C_6H_4] catalysed by the $\text{Pt}(\text{COD})_2$ or $\text{Me}_2\text{Pt}(\text{COD})$ complexes affords polysilanes with high molecular weights (M_w up to 40 000; M_n up to 39 000) in 60%–95% yields.¹⁵⁹

Dehydrocondensation of dimethylphenylsilane in the presence of platinum complexes with different phosphine ligands was

studied.¹⁶⁰ Their catalytic activities are rather low. The exception is the $\text{Pt}(\text{PPhMe}_2)_4$ complex in the presence of which the yield of 1,1,2,2-tetramethyl-1,2-diphenyldisilane reaches 50%. Methylphenylsilane in the presence of $\text{Pt}(\text{PPhMe}_2)_4$ forms 1,2-dimethyl-tetraphenyldisilane in low yield.¹⁶⁰ Platinum black as well as PtO_2 , $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $(\text{PhCN})_2\text{PtCl}_2$ do not catalyse dehydrocondensation of dimethylphenylsilane.¹⁶⁰

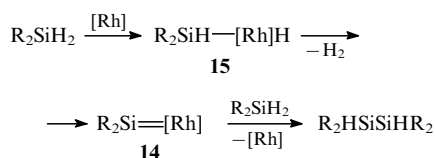
A procedure for the dehydrocondensation of substituted oligosilanes of the general formula $\text{H}_a\text{Si}_b\text{R}_c$ [$\text{R} = \text{Alk}$, Ar , alkenyl, AlkO , Hal or R_2N ; $a \geq 1$; $b \geq 2$; $(a + c) = (2b + 2)$] in the presence of dialkylidicyclopentadienyl Pt or Rh complexes was covered by a patent.⁸³

In 1973, $(\text{Ph}_3\text{P})_3\text{RhCl}$ (Wilkinson's complex) was suggested as a catalyst of dehydrocondensation of hydrosilanes.¹⁰⁸ In its presence, methylphenylsilane was converted into a mixture of 1,2-dimethyl-1,2-diphenyldisilane (14%) and 1,2,3-trimethyl-1,2,3-triphenyltrisilane (30%) at 70 °C for 1 h. Under analogous conditions, 1,1,2,2-tetraphenyldisilane was formed from diphenylsilane in 38% yield. 1,2-Diphenylsilane and 1,2,3-triphenyltrisilane were obtained from phenylsilane. 1,1,2,2-Tetraethylidisilane and 1,1,2,2,3,3-hexaethyltrisilane were obtained from diethylsilane. Dehydrocondensation of dibenzosilaheterocycles **5a–d** in the presence of $(\text{Ph}_3\text{P})_3\text{RhCl}$ proceeds according to the following scheme^{108, 112, 161}



The drawback of Wilkinson's catalyst is the fact that it promotes oxidation of Si–Si bonds to Si–O–Si groups when the reaction is performed in air.^{109, 113}

The possible reaction mechanism involves the formation of the silylene rhodium(II) complex **14** as an intermediate, which appears as a result of β -elimination of the hydrogen molecule from the rhodium(I) complex **15**.



The results of dehydrocondensation of disubstituted silanes in the presence of $(\text{Ph}_3\text{P})_3\text{RhCl}$ are given in Table 2.¹¹² The conversion of R_2SiH_2 decreases in the series **5c,d** (100%) > **5a** (83%) > Ph_2SiH_2 (59%) > **5b** (10%).¹¹³ The addition of cyclohexene as an acceptor of hydrogen does not affect the activity of silanes. In attempting to perform dehydrocondensation of dihydrosilaanthracene (**5a**) in the presence of the $[\text{Rh}(\text{COD})(\text{PPh}_3)_2]\text{PF}_6$ complex (37 °C, 25 h), only the corresponding disiloxane was isolated in 33% yield.¹¹²

Dehydrocondensation of methylphenylsilane catalysed by different rhodium complexes has been studied. In these reactions, a dimer and a trimer were obtained as by-products (Table 3).⁵⁰

Table 2. Dehydrocondensation of diorganylsilanes in the presence of Wilkinson's catalyst (0.4 mol. %, 10 h, 25 °C).¹¹²

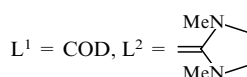
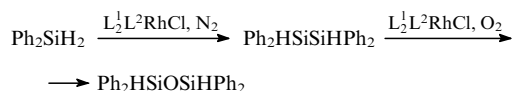
R_2SiH_2	Yield of the reaction products (%)				
	R_2SiH_2	dimer	trimer	disiloxane	other products
Ph_2SiH_2	41	48			11% (Ph_3SiH)
5a	17	38	42	3	
5b	90	10			
5c					oligomer
5d					oligomer

Table 3. Dehydrocondensation of methylphenylsilane in the presence of rhodium complexes (0.1 mol. %).⁵⁰

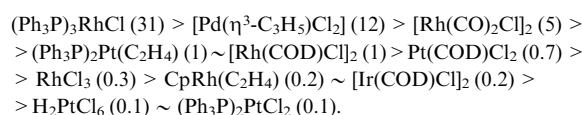
Catalysts	Cocatalyst	t/h	$T/^\circ\text{C}$	Yield (%)		
				MePhSiH_2	dimer	trimer
$\text{RhCl}(\text{PPh}_3)_3$		1	80	65.5	16.3	3.9
	PPh_3	1.5	90	29.3	15.4	6.9
$\text{RhH}(\text{PPh}_3)_4$		2	100	58.5	14.3	4.0
	PPh_3	2	100	29.3	10.3	4.1
	PPh_2Me	2	100	19.2	16.7	3.7
$\text{Rh}_2(\text{OAc})_4$		2	100	69.0	3.3	0
$[\text{RhCl}_4(\text{H}_2\text{O})_2]^- \text{X}^+$ (see ^a)		2	100	31.2	25.8	8.8

^a $\text{X} = \text{NH}(\text{C}_8\text{H}_{13})_3$.

Dehydrocondensation of diphenylsilane catalysed by carbene rhodium complexes (20 °C, 18 h) afforded predominantly 1,1,2,2-tetraphenyldisilane.¹⁶² The reaction was monitored by GLC. It was demonstrated that the disilane $\text{Ph}_2\text{HSiSiHPh}_2$, which was initially formed, was then oxidised by atmospheric oxygen to the corresponding disiloxane.



Hydrosilylation with diethylsilane catalysed by complexes of Group VIII metals involves the dimerisation of diethylsilane as a competitive process. The relative rate constants of dehydrocondensation of diethylsilane (18 °C, 75 h) depending on the catalyst were determined.¹⁰⁹ These constants change in the following order (k_{rel} are given in parentheses):



The reactivity of silanes in dehydrocondensation decreases in the series $\text{RSiH}_3 > \text{R}_2\text{SiH}_2 \gg \text{R}_3\text{SiH}$. Dimethylphenylsilane in the presence of platinum complexes undergoes only dimerisation.

Dehydrocondensation of compounds of the $\text{A}(\text{SiH}_3)_2$ type [$\text{A} = \text{CH}_2$, $\text{Alk}(\text{CH}_2)_n$, $\text{Me}_3\text{Si}(\text{CH}_2)_n$ ($n = 2-7$) or $\text{Me}_3\text{Si}(\text{CH}_2)_m$ ($m = 3-8$)] catalysed by $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ was studied. The reactions afforded polysilanes, which were further converted into silicon carbide.¹⁶³

Dehydrocondensation of 1,4-bis(trihydrosilyl)benzene in the presence of $\text{RuCl}_2[\text{P}(\text{C}_6\text{H}_4\text{Me-4})_3]_3$ afforded a white polymer ($M = 1170$) containing alternating $\text{SiH}_2\text{C}_6\text{H}_4$ groups.^{164, 165}

5. Reaction mechanism

Dehydrocondensation of organylsilanes is a promising procedure for the formation of Si–Si bonds. This procedure is suitable for the preparation of polyorganylsilanes with the controlled chain length. However, the majority of the published studies generally dealt with the preparative aspects of this reaction. The difference in the reaction conditions and sometimes the contradictory results do not allow one to propose the mechanism of catalytic dehydrocondensation of organylhydrosilanes with assurance.

Presently, three rather justified schemes of the process proceeding in stages are available. These schemes are interrelated and complement each other.

1. Harrod's mechanism involves oxidative addition of organylsilanes to complex-forming metal followed by α -elimination of

the RH molecule ($R = \text{Alk}$ or Ar) to form a silylene complex of the $\text{Cp}_2\text{M}=\text{SiHR}$ type ($M = \text{Ti}$ or Zr) as an active catalytic intermediate. The latter forms polyorganylsilanes through a series of successive conversions with the participation of organylsilane.

2. Tilley's mechanism is based on the metathesis of the σ -bond. The reaction proceeds through a four-centre transition state containing the $M-H$, $M-Si$, $Si-H$ and $Si-Si$ bonds followed by the metathesis of the $M-Si$ σ -bond and the formation of dehydrocondensation products $\text{H}(\text{SiHR})_n\text{H}$.

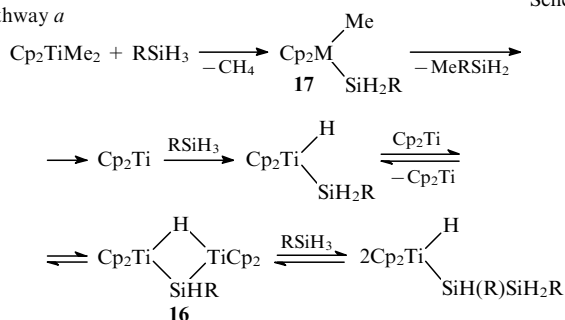
3. Hengge's mechanism involves silylene $\text{Me}_2\text{Si:}$, which is formed in a four-centre transition state according to a β -elimination reaction of a new type, as an active catalytic intermediate. Dimethylsilylene is then inserted into the $Si-H$ or $Si-Si$ bonds to form linear or branched oligomers, respectively.

Let us consider these mechanisms in more detail.

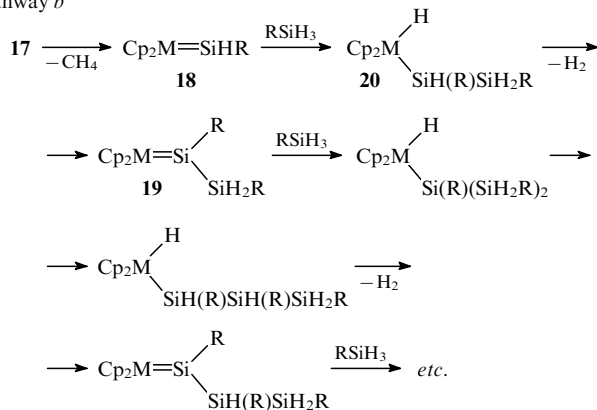
Harrod and coworkers^{68, 87, 89, 93} suggested two schemes of the dehydrocondensation mechanism for organylsilanes (Scheme 2).

One of the schemes⁸⁷ assumes that the bridging hydride complex **16** is formed as an active catalytic intermediate. This scheme involves oxidative addition of silane to metallocene to form the complex **17** followed by α -elimination of MeRSiH_2 . The resulting Cp_2Ti reacts with silane to give the complex **16**, which accomplishes the chain growth (Scheme 2, pathway *a*).

Pathway *a*



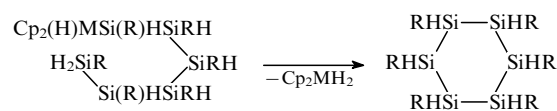
Pathway *b*



However, the high catalytic activity of possible intermediates of dehydrocondensation, *viz.*, the Ti and Zr complexes of type **17** containing $\mu\text{-H}$ and $\mu\text{-Si}$ bonds, was not confirmed.^{87, 89, 91, 94, 100}

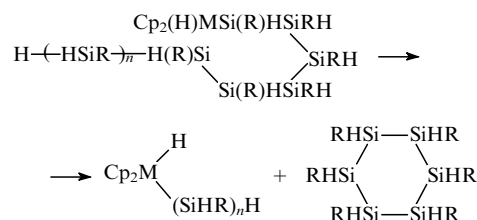
Later on, Harrod and coworkers⁹³ suggested that the silylene complexes **18** and **19** are intermediates in dehydrocondensation. The complex **19** can be formed upon elimination of hydrogen from the hydride complex **20**. The chain growth occurs through the repeated insertion of the newly formed silylene complex into the $M-Si$ bond (Scheme 2, pathway *b*). This scheme adequately describes the formation of the linear polyphenylsilanes $\text{H}(\text{PhSiH})_n\text{H}$ and $\text{H}(\text{Ph}_2\text{Si})_2\text{H}$ from PhSiH_3 and Ph_2SiH_2 , respectively.

The formation of cyclic products upon dehydrocondensation of PhSiH_3 and $\text{PhCH}_2\text{SiH}_3$ in the presence of dimethyltitanocene or dimethylzirconocene proceeds through the intermolecular metathesis of the terminal SiH_2 group and the $M-Si$ bond of the growing terminus of the chain.⁶⁸ This process is most probable when the chain contains six Si atoms.



$M = \text{Ti, Zr}$.

The second pathway, which involves the cleavage of the $Si-Si$ bond by a particular reactive intermediate and intermolecular metathesis, is also possible.



$M = \text{Ti, Zr}$.

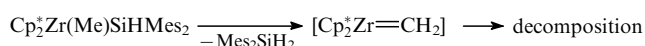
The scheme proposed by Harrod does not explain why only tetraorganylsilanes rather than higher oligomers are formed from diorganylsilane.

An alternative reaction mechanism was proposed¹¹² to account for the formation of cyclic oligomers, for example, of 1,2,3-triphenyltrisilane from Ph_2SiH_2 in the presence of titanocene or zirconocene complexes. This mechanism involves either dehydrocondensation of Ph_2SiH_2 with the resulting $\text{Ph}_2\text{SiHSiHPh}_2$ (which is formed, probably, through a silylene complex) or disproportionation of 1,1,2,2-tetraphenyldisilane.

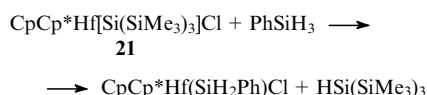
However, it was established¹⁶¹ that the dimeric product of dehydrocondensation of 9,10-dihydro-9-silaanthracene in the presence of Wilkinson's catalyst formed the corresponding trimer only in 7% yield, *i.e.*, disproportionation is not the major process.

Silylene complexes of type **18** or **19** are very attractive compounds for explaining the mechanism of dehydrocondensation of silanes. These compounds have been extensively studied in the last decade.¹⁶⁶ Base-stabilised silylene complexes of transition metals, which are used in different catalytic (hydrosilylation¹⁰⁸) and photochemical¹⁶⁷ reactions, are known.

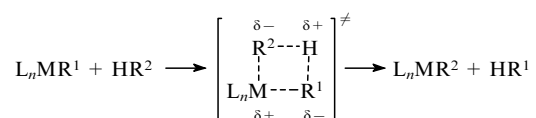
Nevertheless, it is believed⁴⁶ that silylene metal complexes cannot be intermediates of dehydrocondensation for two reasons. First, during catalytic dehydrocondensation of organylsilanes, complexes of the $\text{CpCp}^*\text{M}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ type are quantitatively converted into the corresponding polymeric complexes $[\text{CpCp}^*\text{MHCl}]_n$.¹⁴² Only one σ -bond of complex-forming metal is used in the course of dehydrocondensation. At the same time, the participation of at least two σ -bonds is necessary for the formation of the silylene complex followed by its reaction. Second, the formation of silylene complexes through α -elimination of the RH molecule should result in complexes of the $\text{M}(\text{SiHR}^1\text{R}^2)\text{R}^3$ type (R^1, R^2 and $\text{R}^3 = \text{H}$ or Alk). Several mixed alkylsilyl complexes containing $Si-H$ bonds were isolated. However, the latter do not undergo decomposition with α -elimination of substituents at the silicon atom. Only one instance where decomposition proceeds through α -elimination of the hydrogen atom from the alkyl group at the silicon atom is known.¹⁶⁸ This reaction afforded dimesitylsilane in quantitative yield along with an unidentified zirconium-containing compound. Methane was not detected among the reaction products.



Tilley¹³⁶ suggested an alternative mechanism of dehydrocondensation of organylsilanes, which was called the metathesis of the σ -bond. This mechanism was confirmed by the kinetic data obtained by monitoring the process by ^1H NMR spectroscopy in C_6D_6 .^{46, 48, 142, 169} In this case, the cyclopentadienyl tris(trimethylsilyl) hafnium complex **21**, which exhibits lower reactivity and higher stability compared to the isostructural titanium and zirconium complexes, was used as a catalyst.



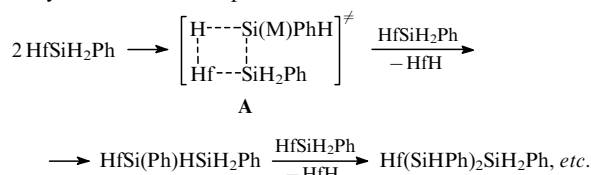
These authors also synthesised and studied the behaviour of other silylated cyclopentadienyl hafnium complexes, *viz.*, $\text{CpCp}^*\text{Hf}(\text{SiHR}^1\text{R}^2)\text{Cl}$ ($\text{R}^1 = \text{H}$ and $\text{R}^2 = \text{Ph}$, 4-MeC₆H₄, Mes, Bn or *cyclo*-C₆H₁₁; $\text{R}^1 = \text{R}^2 = \text{Ph}$; or $\text{R}^1 = \text{Me}$ and $\text{R}^2 = \text{Ph}$), in dehydrocondensation of PhSiH₃.^{141, 170} The general second order of the reaction, first order with respect both to the catalyst and the organylsilane, were established. The activation parameters of the process ($\Delta H^\ddagger = 68.5 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -27 \text{ kJ mol}^{-1} \text{ K}^{-1}$) and the kinetic isotopic effect ($k_{\text{H}}/k_{\text{D}} = 2.5$) correspond to the values observed for the reactions of hydrocarbons proceeding through the metathesis of the σ -bond.^{170, 171}



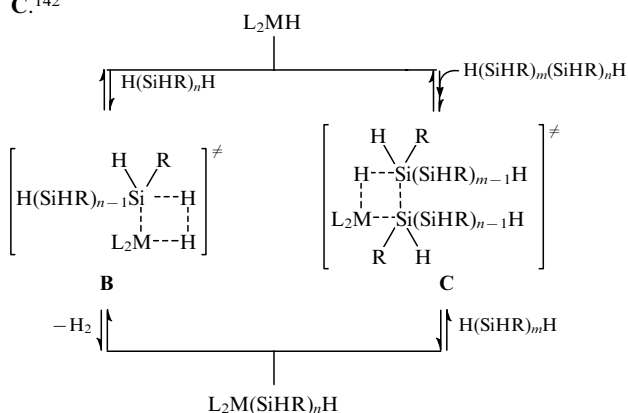
$\text{R}^1, \text{R}^2 = \text{H}, \text{Alk}, \text{Ar};$

$\text{L}_n\text{M} = \text{Cp}_2^*\text{Sc}, \text{Cp}_2^*\text{Y}, \text{Cp}_2^*\text{Lu}, [(\text{Me}_3\text{Si})_2\text{N}]_3\text{U}, \text{etc.}$

The kinetics of thermal decomposition of $\text{CpCp}^*.\text{Hf}(\text{SiH}_2\text{Ph})\text{Cl}$, which obeys a second-order equation with $\Delta H^\ddagger = 81.5 \text{ kJ mol}^{-1}$ and $S^\ddagger = -21 \text{ kJ mol}^{-1} \text{ K}^{-1}$, was studied.¹⁴² The four-centre transition state **A** was suggested for the dehydrocondensation process.



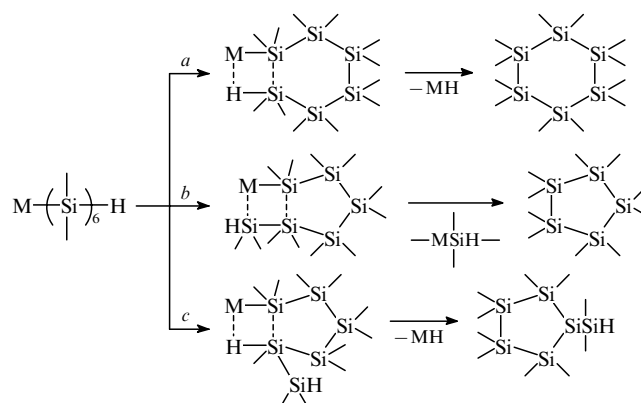
Decomposition of the hafnium complex was performed in the presence of efficient traps of silylene, such as Et₃SiH, (cyclo-C₆H₁₁)₃SiH, Ph₂SiH₂ or MePhSiH₂, which had no effect on the reaction rate. It is suggested that a hydride complex, which reacts predominantly with the sterically most accessible terminal SiH₂R group of the polysilane chain, is an active catalytic species in the reaction. This leads to the appearance of the polysilyl group in the coordination sphere about the metal atom. The formation of the Si–Si bonds (chain growth) occurs through the two-stage metathesis of the σ -bond *via* the four-centre transition states **B** and **C**.¹⁴²



Slow oligomerisation of phenylsilane catalysed by $\text{CpCp}^*.\text{Hf}(\text{SiH}_2\text{Ph})\text{Cl}$ was used as a model reaction. In this process, intermediates of dehydrocondensation, for example, $\text{CpCp}^*\text{Hf}(\text{SiHPhSiH}_2\text{Ph})\text{Cl}$, were identified. This complex was prepared by independent synthesis from $\text{CpCp}^*\text{Hf}[\text{Si}(\text{SiMe}_3)_3]\text{Cl}$ as two diastereomers, which were detected in the course of the reaction by ¹H NMR spectroscopy. The addition of two equivalents of phenylsilane to $\text{CpCp}^*\text{Hf}(\text{SiH}_2\text{Ph})\text{Cl}$ afforded (after

24 h) $[\text{CpCp}^*\text{HfHCl}]_n$ (33%) and a mixture of $\text{CpCp}^*\text{Hf}[\text{SiH}(\text{Ph})\text{SiH}_2\text{Ph}]\text{Cl}$, $\text{PhH}_2\text{SiSiH}_2\text{Ph}$ and $\text{PhH}_2\text{Si}-\text{SiH}(\text{Ph})\text{SiH}_2\text{Ph}$ in a ratio of 3:2:3. Dehydrocondensation of PhSiH₃ catalysed by Cp^*HfH_2 afforded also free oligophenylsilanes. Due to steric hindrance, this hafnium hydride reacts with the Si–H bond very slowly, which makes it possible to observe the conversion of phenylsilane into 1,2-diphenyldisilane. The latter is even more slowly converted into 1,2,3-triphenyltrisilane, and apparently, finally into 1,2,3,4-tetraphenyltetrasilane. The correlation between the concentration of the silane and the reaction time indicates that the cleavage of the Si–Si bond is an important stage of the process. Within the framework of this mechanism, the formation of cyclic oligomers is attributed to the intramolecular metathesis of $\text{R}(\text{RSiH})_n\text{H}$, where $n = 5$ (Scheme 3).¹²⁷ The metathesis with the participation of the terminal Si–H (pathway *a*) or Si–Si (pathway *b*) bonds affords five- or six-membered rings. The metathesis with the participation of the exocyclic Si–H bonds (pathway *c*) can lead to rings containing organosilicon substituents.

Scheme 3



The suggested multistage mechanism of dehydrocondensation of organylsilanes can serve as the basis for the design of new catalysts, *viz.*, coordinatively unsaturated electrophilic metal hydride complexes, which can participate in the concerted process of metathesis of the σ -bond.

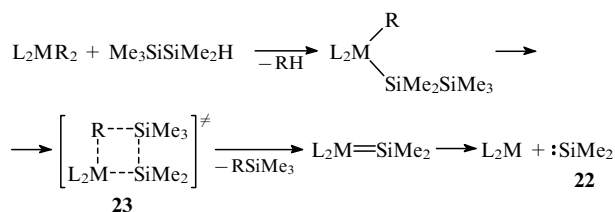
The proposed mechanism explains many aspects of dehydrocondensation, including steric requirements imposed on the catalyst and the substrate as well as the formation of rather short polymer chains. However, this mechanism inadequately explains the difference in the behaviour of, on the one hand, the silyl complexes of zirconium and hafnium and, on the other hand, of the titanium complexes.

The mechanism of metathesis of the σ -bond was also used for the explanation of the regularities of other dehydrocondensation reactions, *viz.*, the reaction of RSiH_3 catalysed by the $\text{Cp}_2\text{MCl}_2-2\text{BuLi}$ binary system or Cp_2MMe_2 ,¹²⁹ the reaction of $\text{R}^1\text{R}^2\text{SiH}_2$ in the presence of Wilkinson's complex¹¹² and the reaction of 2,4-disilapentane in the presence of titanocene or zirconocene.⁴³

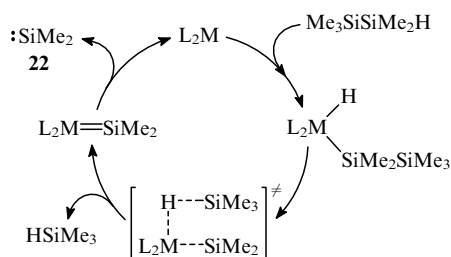
Hengge and Weinberger¹⁷² suggested yet another mechanism of dehydrocondensation of organylsilanes in the presence of dimethylzirconocene with the use of autocondensation of 1,2,3-trimethyltrisilane and a mixture of diastereomers of 1,2,3,4-tetramethyltetrasilane as a model reaction. The conversions of these oligomers cannot be explained in the context of Harrod's mechanism^{87, 89} because α -elimination should be accompanied by evolution of CH₄.

Dimethylsilylene $\text{Me}_2\text{Si}:$ was suggested as an intermediate in dehydrocondensation of $\text{Me}_3\text{SiSiMe}_2\text{H}$ and $\text{HMe}_2\text{SiSiMe}_2\text{H}$ in the presence of Cp_2ZrMe_2 (**22**, Scheme 4). This intermediate is formed from the intermediate silyl metal complex **23** as a result of β -elimination. This process is not the classical elimination of an organic substituent at the β position with respect to the metal atom. This mechanism can more likely be considered as β -bonding

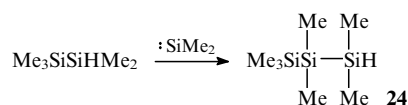
Scheme 4
Pathway a. Formation of the active catalytic L_2M molecule



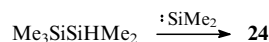
Pathway b. Dehydrocondensation



Pathway c. Insertion of silylene into the Si–H bond



Pathway d. Insertion of silylene into the Si–Si bond

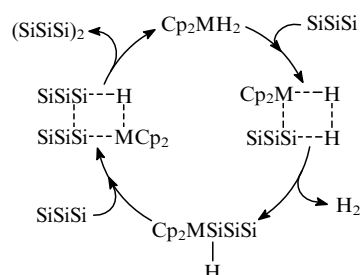


upon destruction of a four-centre transition state accompanied by elimination of the resulting residue, *viz.*, the so-called elimination of the β -bond (Scheme 4, pathways *a,b*). The resulting dimethylsilylene can be inserted both into the Si–H bond (Scheme 4, pathway *c*) and into the Si–Si bond (Scheme 4, pathway *d*) of the initial pentamethyltrisilane to form the heptamethyltrisilane **24**.

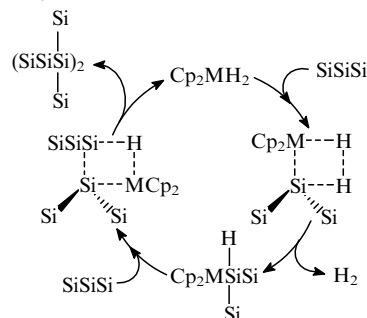
Two pathways of dehydrocondensation of diorganylsilanes and higher silanes are possible, *viz.*, the metathesis of the σ -bond resulting in the formation of linear polymers with evolution of H_2

Scheme 5

Pathway a. Linear metathesis of the σ -bond of $H(MeHSi)_3H$



Pathway b. Branched metathesis of the σ -bond of $H(MeHSi)_3H$



(Scheme 5, pathway *a*) or the β -elimination with evolution of $MeSiH_3$ (Scheme 5, pathway *b*) to form a branched polymer.

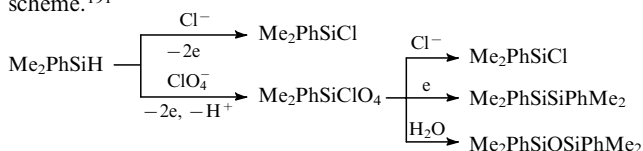
We believe that the mechanism suggested by Tilley,⁴⁶ which is based both on the kinetic data and on the identification of the intermediate reaction products, is the most probable one among the above-considered mechanisms of catalytic dehydrocondensation of organylsilanes. The mechanism suggested by Hengge¹⁷² attracts attention because it involves a new type of elimination reactions, *viz.*, the elimination of the β -bond.

III. Electrochemical dehydrocondensation of organylhydrosilanes

Electrochemical reactions are used for the synthesis of various organosilicon compounds, including functionally substituted compounds.¹⁷³ Methods for the cathodic electroreduction of organylchlorosilanes to form substituted disilanes^{174–177} and oligo- and polysilanes^{178–182} have been developed. Since organylchlorosilanes are difficult to reduce, cathodic processes with their participation generally require preliminary electrogeneration of carbanions (or other nucleophiles), which then replace the chlorine atoms bound to the silicon atoms.¹⁷³ Most of cathodic reactions based on organylchlorosilanes are variations of this process.

Anodic reactions of organosilicon compounds are more diversified, though less well studied, than cathodic reduction processes.^{173, 183–186}

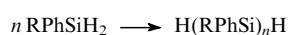
Electroreduction of mono-, di- and triorganylsilanes $RSiH_3$ ($R = Ph$ or $n-C_6H_{13}$), $R^1R^2SiH_2$ (R^1 and $R^2 = Me$ or Ph) and R_3SiH ($R = Et$ or EtO) on metallic (Pt , Au or Hg)^{187–190} and nonmetallic (glassy-carbon)¹⁹¹ electrodes was studied. The reactions were performed in acetonitrile in the presence of Bu_4NBF_4 (see Refs 187–190) or $LiClO_4$.¹⁹¹ Organylsilanes have low oxidation potentials on metallic electrodes (the $E_{Red/Ox}$ value varies from -0.05 to 0.7 V). On the contrary, the oxidation potential of dimethylphenylsilane on a glassy-carbon electrode is rather high ($E_{Red/Ox} = 2.2$ V). Preparative electrooxidation of Me_2PhSiH in the DME– Bu_4NClO_4 system (DME is dimethoxyethane) in the presence of $CuCl$ or $CuCl_2$ affords a mixture of compounds. The formation of the latter can be described by the following scheme.¹⁹¹



Chlorodimethylphenylsilane is formed in a yield from 46% to 95% depending on the degree of oxidation of copper and the quantity of electricity passed. Under these conditions, 1,1,2,2-tetramethyl-1,2-diphenyldisilane is formed in insignificant yield. When the supporting electrolyte was changed for Bu_4NBF_4 , fluorodimethylphenylsilane predominantly formed (the yield was 90%). In this case, the exchange reaction of the initially formed $Me_2PhSiCl$ with BF_4^- apparently proceeded.^{180, 192–194}

The oxidation potentials of the initial monomeric organylsilanes¹⁹⁰ are ~ 200 mV lower than the oxidation potentials of polyorganylsilanes, which hinders oxidation of the latter with the cleavage of the Si–Si bond.¹⁷³

Electrolysis of methylphenyl- and diphenylsilane in the DME– Bu_4NBF_4 system with the use of a platinum cathode and a platinum anode for 5.3 h afforded the corresponding oligomers.^{195, 196}



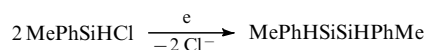
$R = Me: n = 2–6; R = Ph: n = 2–5.$

According to GLC data, the dehydrocondensation product of methylphenylsilane, which is characterised by $M_n = 454$ and the molecular distribution coefficient $M_w/M_n = 1.05$, is a mixture of at least five compounds. 1,2-Dimethyl-1,2-diphenyldisilane

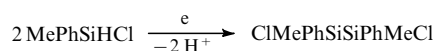
($n = 2$, $M = 242$, the yield was 10%) and 1,2,3-trimethyl-1,2,3-triphenylsilane ($n = 3$, $M = 362$, the yield was 14%) were identified in the reaction mixture by mass spectrometry. The yields of methylphenyloligosilanes with $n = 4$ and 5 were 16% and 6%, respectively.¹⁸⁵ Under analogous conditions, diphenylsilane was predominantly converted into the dimer, *viz.*, 1,1,2,2-tetraphenyldisilane (the conversion was 38%), in 23% yield. Apparently, silyl radical cations are intermediates in this anodic reaction. Then these radical cations attack the corresponding monomers or oligomers to form the Si–Si bond.

Polyorganylsilanes of the $H(RHSi)_nH$ type are formed upon electrolysis of organylsilanes R^1SiH_3 ($R^1 = \text{Alk}$, Ar or $\text{CH}_2\text{CH}_2\text{R}^2$, where R^2 is a perfluoroalkyl group) in an organic solvent containing an appropriate electrolyte. Previously unknown oligo- and polyfluoroalkylsilanes with $M = 200$ –5000 were synthesised according to this procedure in high yields.¹⁹⁷

Electrolysis of organylchlorosilanes $RSiH_nCl_{3-n}$ ($n = 1$ or 2) in the THF– Bu_4NBF_4 system in an undivided cell yields two different condensation products depending on the metal of the electrodes.¹⁹⁸ Electrolysis of methylphenylchlorosilane with the use of a stainless steel cathode and a subcritical anode affords predominantly 1,2-dimethyl-1,2-diphenyldisilane, which is formed upon cathodic reduction with elimination of chlorine.

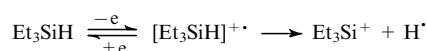


When platinum electrodes are used, the cathodic reduction is suppressed and the anodic oxidation becomes the predominant reaction. In this case, the Si–Si bond is formed through the elimination of the proton on an anode.



Radical cations formed upon electrochemical oxidation of triorganylsilanes R_3SiH were identified as adducts with tetracyanoethylene¹⁹⁹ or cyclohexene.^{188, 189, 200} The lifetime of the radical cation $\text{Et}_3\text{SiH}^{+\cdot}$, which was detected by the rotating disk-ring electrode method, is 0.003–0.006 s.^{188, 189}

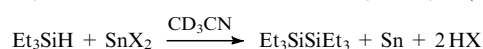
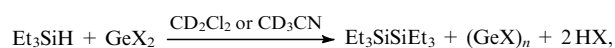
In the absence of radical traps, these radical cations decompose with liberation of the hydrogen atom.



IV. Other reactions

Dehydrocondensation of organylsilanes can also occur under the action of di-*tert*-butyl peroxide.^{201–203} Thus the reaction of dimethylcyclopropylsilane with di-*tert*-butyl peroxide afforded tetramethyl-1,2-di(cyclopropyl)disilane in small yield,²⁰² whereas the reaction of dimethylphenylsilane gave a mixture of $\text{PhMe}_2\text{Si} - \text{SiMe}_2\text{H}$ (2%), $\text{PhMe}_2\text{SiSiMe}_3$ (6%), $\text{Ph}_2\text{MeSiSiMe}_3$ (3%) and $\text{PhMe}_2\text{SiSiMe}_2\text{Ph}$ (3%) in insignificant yield.²⁰³ Disilane was prepared by the reaction of di-*tert*-butyl peroxide with dimethyl(2-thienyl)silane in noticeable yield (26%).²⁰³

Recently, it was found that triethylsilane underwent dehydrocondensation to form hexaethyldisilane in the reaction with germanium or tin dihalides.^{204–206}



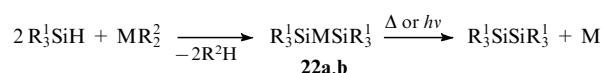
$\text{X} = \text{Cl}, \text{I}$.

The reaction of triethylsilane with tetrachlorogermanium affords a mixture of hexaethyldisilane and triethylchlorosilane in a ratio of 1 : 3.^{204, 205}



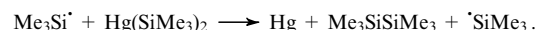
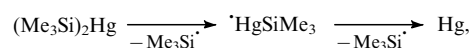
The reactions of germanium dichloride with Et_3SiH proceed readily in more or less polar solvents (CD_3CN or CD_2Cl_2) but do not proceed in nonpolar solvents (C_6D_6). Tetrachlorogermanium reacts with Et_3SiH only in a polar solvent (CD_3CN). It is believed that electron transfer to form the $[\text{Et}_3\text{SiH}^{+\cdot}\text{GeCl}_2^-]$ and $[\text{Et}_3\text{SiH}^{+\cdot}\text{GeCl}_4^-]$ radical ion pairs, respectively, is the key stage of these reactions.

Thermal and photochemical decomposition of bis(triorganylsilyl)mercury and -cadmium **22a,b** can be considered as a two-stage procedure for the dehydrocondensation of triorganylsilanes to form hexaorganyldisilanes.^{207–212} The compounds **22a,b** were prepared by the reactions of triorganylsilanes with dialkyl derivatives of mercury and cadmium.^{207, 209, 213}

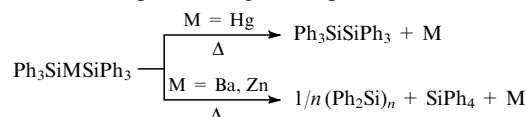


$\text{M} = \text{Hg (a)}, \text{Cd (b)}$.

The reaction proceeds according to the radical mechanism through intermediate formation of the $R_3\text{Si}^{\cdot}$ radicals.^{214–217} The latter not only can undergo recombination but also can react with the solvent (particularly, in a photochemical process).^{213, 218–220}



Thermolysis of bis(triphenylsilyl)mercury, -zinc and -barium derivatives proceeds with elimination of free metal.²¹⁰ Hexaphenyldisilane is formed from the mercury derivative. The barium and zinc compounds give tetraphenyldisilane and diphenylsilylene. The latter undergoes subsequent oligomerisation.²¹²



Bis(methyldichlorosilyl)- and bis(dimethylchlorosilyl)-mercury, which were prepared under UV irradiation of a mixture of bis(trimethylsilylmethyl)mercury and the corresponding methyldichloro- or dimethylchlorosilane, spontaneously decompose above -79°C with elimination of mercury to form substituted disilanes.²¹²

V. Conclusion

To summarise, dehydrocondensation of organosilicon compounds containing Si–H bonds is a promising procedure for the preparation of linear and cyclic oligo- and polyorganylsilanes $H(R^1R^2Si)_nH$ and $-(\text{SiR}^1\text{R}^2)_n-$, which find use as precursors of ceramics, semiconductors, photoresistors, photoinitiators of polymerisation of alkenes, *etc.*

Group IVB metallocenes Cp_2ML_2 ($\text{M} = \text{Ti}, \text{Zr}$ or Hf ; $\text{L} = \text{H}$, Alk , OAlk , Ar or Hal) and their binary systems with promoters, such as alkylolithium, triorganylphosphines, aluminium, *etc.*, are the most efficient catalysts of dehydrocondensation. These compounds allow one to prepare linear and cyclic polysilanes under rather mild conditions. The catalytic activity of metallocenes decreases in the $\text{Zr} > \text{Ti} \gg \text{Hf}$ series depending on the nature of the central metal atom. When heteronuclear metallocenes are used, monosilanes RSiH_3 are more active than diorganylsilanes R_2SiH_2 , while triorganylsilanes R_3SiH do not undergo dehydrocondensation.

As for the mechanism of dehydrocondensation, it is evidently nontrivial and complicated. Apparently, further studies will be aimed at elucidating details of the mechanism, which can allow one to elaborate an approach to the choice of catalysts for the purpose of enhancing the selectivity of a procedure for the preparation of polysilanes with the desired structures.

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Free radical addition: factors determining the activation energy

E T Denisov

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Abstract. Empirical relations describing the reactivity of reagents in radical addition reactions and the results of quantum-chemical calculations of the activation energy of these processes are considered. The experimental data obtained for the addition of atoms and radicals to molecules with multiple bonds are analysed in terms of the parabolic model. The following characteristics and factors are shown to affect the activation energy of radical addition: the reaction enthalpy, the strength of the arising bond, the radius of the atom having a free valence, the presence of a π bond adjacent to the reaction centre, the interaction of two polar groups, the multidipole interaction, the steric factor, the non-linearity of the reaction centre, and the force constants of the reacting bonds. The bibliography includes 85 references.

I. Introduction

Radical addition to unsaturated compounds underlies the modern technology for production of polymers, copolymers and oligomers.^{1–5} These reactions proceed during pyrolysis of hydrocarbons, halogenation of alkenes or oxidation of unsaturated compounds.^{6–9} They are widely used in the synthesis of diverse medicines.^{10–14} The addition of hydrogen atoms and hydroxyl radicals to unsaturated, aromatic and heterocyclic compounds is involved in the photolysis and radiolysis of organic materials and biological objects.⁷ The problem of reactivity of compounds in the addition of atoms and radicals to double $C=C$ bonds has been widely discussed and is still debated.^{3, 6, 8, 15–24} Two factors which exert substantial influence on these processes have been noted,

namely, heat (enthalpy) of the reaction and the interaction of polar groups of the reactants in the transition state (the so-called polar factor). Quantum-chemical calculations showed that the reaction centre in the transition state is non-linear.¹⁶ When interpreting the results of these calculations, researchers restricted themselves to consideration of only three factors influencing the activation energy of addition, namely, the reaction enthalpy, the interaction of polar groups and the steric effect.^{25–39}

Analysis of the experimental data (on activation energies) obtained in the studies of radical abstraction reactions in terms of the parabolic model showed that, apart from the factors mentioned above, there is a whole series of other factors that determine the activation energy of an elementary step.^{40–42} The author of this review has analysed an extensive array of experimental data concerning radical addition reactions in terms of the parabolic model for this type of reaction.^{43–53} The results of this analysis are presented in detail in this review.

II. Enthalpy and entropy of radical addition

The radical addition reactions



involve the rupture of the $C=C$ π bond and the formation of a $C-X$ σ bond. A σ bond is normally stronger than a π bond; hence, radical addition is an exothermic reaction. This can be clearly seen when comparing the reaction enthalpies ΔH and the strengths of the bonds being formed $D(Et-X)$ given in Table 1; the stronger the $Et-X$ bond, the larger the $-\Delta H$ value. Yet another important factor influencing the reaction enthalpy is the energy of stabilisation of the radical $XCH_2C^{\cdot}HY$ formed: the higher this energy, the greater the heat of the addition of the $X^{\cdot}$ radical to an alkene. Stabilisation energy can be characterised as the difference between the strengths of the $C-H$ bonds in $Pr-H$ and $EtYHC-H$. Below we present the data characterising the contribution to the enthalpy of this reaction of the stabilisation

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Table 1. Bond strength (kJ mol^{-1}), enthalpy (kJ mol^{-1}), entropy ($\text{J mol}^{-1} \text{K}^{-1}$) and Gibbs energy (kJ mol^{-1}) for the addition of atoms and $X^\bullet$ radicals to ethylene ($T = 298 \text{ K}$).

$X^\bullet$	$D(\text{Et}-X)$	$-\Delta H$	$-\Delta S$	$-\Delta G$
$\text{H}^\bullet$	422	150	84	125
$\text{Cl}^\bullet$	352	82	88	56
$\text{C}^\bullet\text{H}_3$	370	100	122	64
$\text{Me}_2\text{C}^\bullet\text{H}$	364	92	134	52
$\text{PhC}^\bullet\text{H}_2$	318	63	122	27
$\text{N}^\bullet\text{H}_2$	353	81	109	49
$\text{HO}^\bullet$	343	122	100	93
$\text{CH}_3\text{O}^\bullet$	352	82	118	46
$\text{HO}_2^\bullet$	327	63	134	23

energy of the $\text{MeCH}_2\text{C}^\bullet\text{HY}$ radical, resulting from the addition of a methyl radical to the monomer $\text{CH}_2=\text{CHY}$.

Y	H	C(O)OMe	Cl	CN	Ph
$D_{\text{Pr-H}} - D_{\text{EtYHC-H}}$ / kJ mol^{-1}	0.0	23.2	24.1	33.6	57.9
$-\Delta H / \text{kJ mol}^{-1}$	95.8	102.0	104.3	129.7	143.0

It can be seen that the greater the energy of radical stabilisation, the smaller the reaction enthalpy.

All the addition reactions are accompanied by a decrease in entropy (two species are combined to give one species, see Table 1). Therefore, for addition reactions, $\Delta G < \Delta H$ (ΔG is the Gibbs energy) and, when the temperature is sufficiently high, exothermic addition is reversible because $\Delta G = \Delta H - T\Delta S$.

Free radical addition can be considered to be reversible if the equilibrium concentration of the $X^\bullet$ radicals is commensurate with the concentration of the $\text{XCH}_2\text{C}^\bullet\text{HY}$ radicals formed, i.e. if the $[\text{X}^\bullet]:[\text{XCH}_2\text{C}^\bullet\text{HY}]$ ratio in the equilibrium state is not smaller than 0.05. When $[\text{CH}_2=\text{CHY}] = 10 \text{ mol litre}^{-1}$ and $T = 300 \text{ K}$, this condition results in the inequality $K \geq 200$ (K is the equilibrium constant). In turn, $-RT \ln K = \Delta G$; therefore, $\Delta G \leq -RT \ln 200 = -13 \text{ kJ mol}^{-1}$. For addition reactions, $\Delta S \approx -100 \text{ J mol}^{-1} \text{K}^{-1}$; therefore, the enthalpy of irreversible addition of $X^\bullet$ to an alkene

$$\Delta H = \Delta G + T\Delta S$$

should be smaller than -43 kJ mol^{-1} (at $T = 300 \text{ K}$).

The ΔH values for radical addition reactions listed in Table 1 comply with this condition. Naturally, as the temperature rises, the boundary value of ΔH increases in absolute magnitude.

III. Empirical correlation equations

Activation energy and heat of reaction. A linear correlation between the change in the activation energy (ΔE) of the monomer addition to a macroradical and the change in the heat of the reaction (Δq) of the type

$$\Delta E = -\alpha' \Delta q, \quad (1)$$

where α' is an empirical factor of proportionality, was found by Evans *et al.*⁵⁴ Later, N N Semenov confirmed this correlation and extended it to a wider range of addition reactions.¹⁵ However, even for a narrow series of reactions, for example, for the addition of methyl radical to $\text{CH}_2=\text{CHY}$, this correlation is nothing but a trend. Indeed, the correlation coefficient for the variation of $\Delta \log k$ as a function of Δq is 0.85 (k is the reaction rate constant).⁵⁵ Evidently, apart from the heat of reaction, other factors also influence the activation energy.

The Alfrey and Price $Q-e$ scheme⁵⁶ takes account of two factors affecting activation energy, namely, the energy of stabilisation of the radical formed in the reaction and the interaction

between polar groups in the radical and the monomer. This scheme was based on the analysis of empirical rate constants for copolymerisation. The rate constant for the reaction of a radical with a monomer is postulated to have the following form:

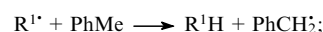
$$k_{12} = P_1 Q_2 \exp(-e_1 e_2), \quad (2)$$

where the factors P_1 and Q_2 reflect the reactivity and e_1 and e_2 are the charges of the radical and the monomer, respectively. The Q and e parameters are calculated from the corresponding rate constants for copolymerisation. When developing the $Q-e$ scheme, the researchers assumed that the charges on the molecule and on the radical are equal and constant (polarisation in the transition state was not taken into account) and that the copolymerisation rate constants do not depend on the dielectric constant of the medium. Subsequently, these assumptions have been criticised.² The $Q-e$ scheme made it possible to systematise the vast experimental information on radical copolymerisation of various monomers. It permits rough prediction of the rate constants for copolymerisation. The Q and e values for monomers in radical polymerisation are listed in Table 2.

Table 2. Correlation parameters for the reactivity of monomers towards radical polymerisation in terms of the Alfrey–Price (Q , e), Bamford–Jenkins (α , β) and Ito–Matsuda (K , P) schemes.^{56–62}

Monomer	Q	e	α	β	K	P
$\text{CH}_2=\text{CHPh}$	1.00	−0.80	0.00	4.85	2.28	1.00
$\text{CH}_2=\text{CHSEt}$	0.27	−1.33	−0.50	4.21	1.30	2.78
$\text{CH}_2=\text{CHSO}_2\text{Et}$	0.07	1.29	−4.0	4.62	−1.40	−0.26
$\text{CH}_2=\text{CHCO}_2\text{Me}$	0.45	0.60	−3.0	5.20	0.00	0.58
$\text{CH}_2=\text{CHOCOMe}$	0.03	−0.88	0.0	3.00	−1.36	0.81
$\text{CH}_2=\text{CHCN}$	0.48	0.12	−3.0	5.30	0.89	−1.00
$\text{CH}_2=\text{CHOEt}$	0.02	−1.17	0.0	2.97	−0.59	1.63
$\text{CH}_2=\text{CMePh}$	0.98	−0.81	−1.0	4.72	1.30	1.69
$\text{CH}_2=\text{CMeCO}_2\text{Me}$	0.78	0.40	—	4.90	1.89	0.25
$\text{CH}_2=\text{CHCH}=\text{CH}_2$	1.70	−0.50	0.0	5.03	—	1.00
$\text{CH}_2=\text{CMeCH}=\text{CH}_2$	1.99	−0.55	0.0	4.92	—	1.09
$\text{CH}_2=\text{CClCH}=\text{CH}_2$	10.52	1.20	−1.5	5.82	—	0.10
$\text{CH}\equiv\text{CPh}$	0.45	0.5	0.5	4.41	—	1.00

The Bamford and Jenkins $\alpha-\beta$ scheme.⁵⁷ These researchers suggested that the reactivities of a radical and a monomer should be described by three parameters, namely, rate constant for the reaction of the macroradical (for example, $\text{R}^{1\bullet}$) with toluene (k_T)



the product of coefficient α with the Hammett constant σ , which takes into account the polar effect, and the coefficient β , reflecting the difference between the radical reactivities towards the monomer and towards toluene. Thus the equation for the rate constant for the addition of $\text{R}^{1\bullet}$ to the monomer M_1 is represented as follows:

$$\ln k_{11} = \ln k_T + \alpha_1 \sigma_1 + \beta_1; \quad (3)$$

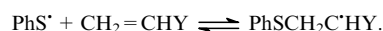
the coefficients σ_1 and β_1 are calculated from the dependence of $\ln(k_{11}/k_T)$ on σ , and the rate constant k_T is determined experimentally at $T = 333 \text{ K}$. The values of α and β for a number of monomers are listed in Table 2.

The relationship between the parameters of the Alfrey–Price and Bamford–Jenkins schemes is expressed by the following equations:⁵⁸

$$-e_1(e_1 - e_2) = \sigma_1(\alpha_1 - \alpha_2), \quad (4)$$

$$\ln Q_1 - \ln Q_2 = \beta_1 - \beta_2.$$

The Ito and Matsuda K - P scheme.^{59–62} In terms of this scheme, the activation energy of an addition reaction is represented as the sum of two terms, E_1 and E_2 . The first term E_1 is proportional to the change in the Gibbs energy in the reversible addition of the thiyl radical $\text{XC}_6\text{H}_5\text{S}^\bullet$ to the monomer, $E_1 \sim \log K$, where K is the equilibrium constant of the reaction



The second term E_2 reflects the contribution of the polar interaction between the radical and the monomer to the activation energy. The contribution of the Gibbs energy to the activation energy is determined by the coefficient present in the linear dependence on $\log K$ of the logarithm of the rate constant (k_X) for the addition of the $\text{XC}_6\text{H}_4\text{S}^\bullet$ radical to the monomer $\text{CH}_2=\text{CHY}$

$$\Delta \log k_X = \alpha_Y \Delta \log K. \quad (5)$$

The α_Y value depends on the nature of the substituent Y in the monomer, this dependence being used to estimate the contribution of the polar effect to the activation energy. This contribution is characterised by the increment P

$$P = \alpha_Y + 2(\alpha_Y - \alpha_{\text{styrene}}). \quad (6)$$

The parameters K and P are listed in Table 2. Parameters of the Ito–Matsuda scheme are related to the parameters of the Alfrey–Price approach by simple relations:⁶²

$$\begin{aligned} \log Q &= 0.49 K - 0.93, \\ e &= 0.91 P + 0.95. \end{aligned} \quad (7)$$

All the above schemes include, in essence, different variants of empirical linear equations in which the rate constants for chain propagation in the free radical polymerisation are brought into correlation with thermodynamic [heat, Hammett constant (σ), the change in the Gibbs energy in the equilibrium reaction] and kinetic (logarithms of the rate constants of the reference reaction and the reaction under study) characteristics of the addition reaction.

IV. Quantum-chemical calculations of the activation energy

Quantum-chemical methods are widely used to study addition reactions.^{26–39} The results obtained, in particular, the activation energies, depend significantly on the programme chosen for calculations. For example, Wong *et al.*³⁸ calculated the activation energy of the methyl radical addition to ethylene using the QCISD(T) programme package. The results of calculations by this programme are in good agreement with experimental data.

When atoms approach one another and a transition state is formed, the bond angles at the carbon atom attacked by an atom or radical substantially change. Figure 1 shows the configuration of atoms in the transition state for the addition of substituted methyl radicals $\text{XC}^\bullet\text{H}_2$ to substituted ethylenes $\text{CH}_2=\text{CHY}$.³⁸ The geometry of the transition state is characterised by the distance $r(\text{C}-\text{C})$, the angle of attack $\varphi_{\text{at}} = \varphi(\text{CCC})$ and the pyramidal angle $\varphi_{\text{pyr}} = \varphi(\text{HCC})$. The last-mentioned parameter

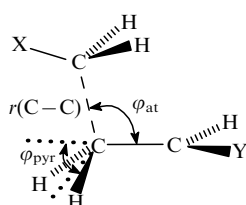


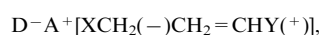
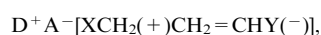
Figure 1. Geometry of the reaction centre in the transition state for the addition of substituted methyl radicals ($\text{XC}^\bullet\text{H}_2$) to substituted ethylenes ($\text{CH}_2=\text{CHY}$).³⁸

Table 3. Interatomic distances and bond angles in the reaction centre and the activation energies for the addition of the $\text{XC}^\bullet\text{H}_2$ radicals to ethylene (quantum-chemical calculations).³⁸

X	$r(\text{C}-\text{C})/\text{\AA}$	$\varphi_{\text{at}}/\text{deg}$	$\varphi_{\text{pyr}}/\text{deg}$	$E/\text{kJ mol}^{-1}$
H	2.246	109.9	25.0	39.8
OH	2.226	108.2	25.9	35.0
CN	2.173	109.3	28.0	42.3

is the angle of deviation of the two $\text{C}-\text{H}$ bonds of ethylene from the plane in which they have been located in the initial molecule (the four hydrogens and both carbons of ethylene lie in one plane). Table 3 presents the values of the three above parameters and the activation energies for the addition of methyl radicals and the $\text{C}^\bullet\text{H}_2\text{OH}$ and $\text{C}^\bullet\text{H}_2\text{CN}$ radicals to ethylene.³⁸

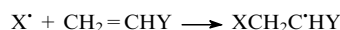
The energy profile of the addition reaction is calculated using specific quantum-chemical programmes as a superposition of four different electron configurations of the reactants, namely,^{38,39}



where D is the radical, A is the molecule, the arrows mark the orientation of the electrons involved in the reorganisation, and $(+)$ and $(-)$ are the charges on the radical and on the molecule. The results (the activation energies) thus obtained are considered with allowance for the influence of two values, namely, the reaction enthalpy and the polar effect.

V. The parabolic model of radical addition

Within the framework of the parabolic model, radical addition



is represented⁴³ as a result of intersection of two potential curves, each of them describing the potential energy of the stretching vibrations of atoms as a parabolic function of the amplitudes of vibrations of atoms in the outgoing (i) and incoming (f) bonds. In terms of the parabolic model, radical addition can be characterised by the following parameters (Fig. 2).

1. Reaction enthalpy ΔH_e

$$\Delta H_e = D_i - D_f + 0.5hL(v_i - v_f) = \Delta H + 0.5hL(v_i - v_f), \quad (8)$$

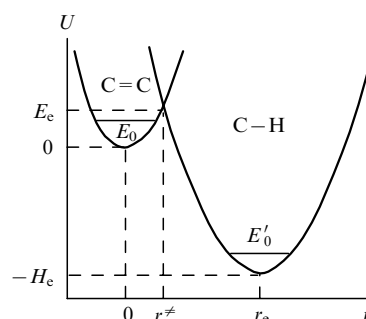


Figure 2. Diagram of the transition state for the hydrogen atom addition to ethylene in the coordinates of the amplitude of the stretching vibration of atoms in the reaction centre (r) and the potential energy of the stretching vibration (U) in terms of the parabolic model.⁴³

E_0, E'_0 are the zero-point energies of the corresponding bonds.

Table 4. Parameters of various classes of addition of atoms and radicals to multiple bonds used in the parabolic model.^{44–50}

Reaction	α	$10^{-11}b /$ $\text{kJ}^{1/2} \text{mol}^{-1/2} \text{m}^{-1}$	$0.5hLv /$ kJ mol^{-1}	$\Delta\Delta H_c /$ kJ mol^{-1}	$10^{-10}A /$ $\text{litre mol}^{-1} \text{s}^{-1}$
$\text{H}^{\bullet} + \text{CH}_2=\text{CHR} \longrightarrow \text{CH}_3\text{C}^{\bullet}\text{HR}$	1.440	5.389	9.9	−7.5	10
$\text{H}^{\bullet} + \text{CH}\equiv\text{CR} \longrightarrow \text{CH}_2=\text{C}^{\bullet}\text{R}$	1.847	6.912	12.7	−4.7	40
$\text{D}^{\bullet} + \text{CH}_2=\text{CHR} \longrightarrow \text{DCH}_2\text{C}^{\bullet}\text{HR}$	1.461	5.389	9.9	−2.7	10
$\text{Cl}^{\bullet} + \text{CH}_2=\text{CHR} \longrightarrow \text{ClCH}_2\text{C}^{\bullet}\text{HR}$	1.591	5.389	9.9	4.8	9
$\text{Br}^{\bullet} + \text{CH}_2=\text{CHR} \longrightarrow \text{BrCH}_2\text{C}^{\bullet}\text{HR}$	1.844	5.389	9.9	5.8	5
$\text{R}^{\bullet} + \text{CH}_2=\text{CHR} \longrightarrow \text{RCH}_2\text{C}^{\bullet}\text{HR}$	1.202	5.389	9.9	1.7	0.1
$\text{R}^{\bullet} + \text{CH}\equiv\text{CR} \longrightarrow \text{RCH}=\text{C}^{\bullet}\text{R}$	1.542	6.912	12.7	3.8	0.1
$\text{N}^{\bullet}\text{H}_2 + \text{CH}_2=\text{CHR} \longrightarrow \text{NCH}_2\text{C}^{\bullet}\text{HR}$	1.410	5.389	9.9	3.1	0.008
$\text{RO}^{\bullet} + \text{CH}_2=\text{CHR} \longrightarrow \text{ROCH}_2\text{C}^{\bullet}\text{HR}$	1.413	5.389	9.9	3.3	0.05
$\text{RO}_2^{\bullet} + \text{CH}_2=\text{CHR} \longrightarrow \text{ROOCH}_2\text{C}^{\bullet}\text{HR}$	1.737	5.389	9.9	4.6	0.1
$\text{R}_3\text{Si}^{\bullet} + \text{CH}_2=\text{CHR}^2 \longrightarrow \text{R}_3\text{SiCH}_2\text{C}^{\bullet}\text{HR}^2$	2.012	5.389	9.9	4.1	0.1
$\text{PhS}^{\bullet} + \text{CH}_2=\text{CHR} \longrightarrow \text{PhSCH}_2\text{C}^{\bullet}\text{HR}$	2.282	5.389	9.9	6.3	0.07
$\text{H}^{\bullet} + \text{O}=\text{CR}^1\text{R}^2 \longrightarrow \text{HOC}^{\bullet}\text{R}^1\text{R}^2$	1.600	5.991	10.3	−11.4	10
$\text{R}^{\bullet} + \text{O}=\text{CR}^1\text{R}^2 \longrightarrow \text{ROC}^{\bullet}\text{R}^1\text{R}^2$	1.570	5.991	10.3	3.7	0.05
$\text{R}_3\text{Si}^{\bullet} + \text{O}=\text{CR}^1\text{R}^2 \longrightarrow \text{R}_3\text{SiOC}^{\bullet}\text{R}^1\text{R}^2$	2.518	5.991	10.3	7.0	0.08

Table 5. Parameters ΔH_c , E_c , br_c and ΔE_H for the hydrogen atom addition to multiple bonds in the gas and liquid phases calculated from Eqns (8)–(10).^{64–79}

Alkene	$\Delta H_c /$ kJ mol^{-1}	Phase ^a	$E_c /$ kJ mol^{-1}	$br_c /$ $\text{kJ}^{1/2} \text{mol}^{-1/2}$	$-\Delta E_H /$ kJ mol^{-1}
$\text{CH}_2=\text{CH}_2$	162.1	gas (4)	22.5	24.26	79.1
$\text{CH}_2=\text{CH}_2$	162.1	liq (2)	22.6	24.32	79.0
$\text{CH}_2=\text{CHMe}$	165.3	gas (1)	21.6	24.34	80.0
$\text{CH}_2=\text{CHMe}$	165.3	liq (1)	20.3	24.08	81.3
$\text{CH}_2=\text{CHEt}$	166.2	gas (1)	20.2	24.15	81.4
$\text{CH}_2=\text{CHEt}$	166.2	liq (1)	19.6	24.01	82.0
$\text{CH}_2=\text{CMe}_2$	168.9	gas (1)	18.0	23.93	83.6
$\text{CH}_2=\text{CHPr}$	165.7	gas (1)	20.6	24.19	81.0
$\text{CH}_2=\text{CHPr}$	165.7	liq (1)	24.3	24.73	77.3
<i>cis</i> -MeCH=CHEt	158.5	gas (1)	23.9	24.34	77.7
<i>trans</i> -MeCH=CHEt	154.2	gas (1)	24.1	24.13	77.5
<i>cis</i> -MeCH=CHEt	158.5	liq (1)	26.9	24.34	74.7
$\text{CH}_2=\text{CMeEt}$	173.3	gas (1)	20.3	24.55	81.3
$\text{CH}_2=\text{CMeEt}$	173.3	liq (1)	23.5	25.00	78.1
$\text{MeCH}=\text{CMe}_2$	169.5	liq (1)	24.4	24.94	77.2
$\text{CH}_2=\text{CMePr}$	173.3	liq (1)	23.3	24.97	78.3
$\text{CH}_2=\text{CEt}_2$	168.9	liq (1)	23.3	24.75	78.3
$\text{EtCH}=\text{CMe}_2$	165.9	liq (1)	24.7	24.80	76.9
$\text{MeCH}=\text{CHPr}$	158.5	liq (1)	25.3	24.50	76.3
$\text{Me}_2\text{C}=\text{CMe}_2$	177.7	liq (1)	25.1	25.48	76.5
$\text{MeCH}=\text{CHBu}$	158.5	liq (1)	25.3	24.51	76.3
$\text{MeCH}=\text{CEt}_2$	163.1	liq (1)	24.5	24.63	77.1
$\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{Me}$	165.7	liq (1)	24.2	24.71	77.4
$\text{CH}_2=\text{CH}(\text{CH}_2)_5\text{Me}$	165.7	liq (1)	24.3	24.74	77.3
$\text{CH}_2=\text{CH}(\text{CH}_2)_7\text{Me}$	165.7	liq (1)	24.2	24.72	77.4
cyclo- C_5H_8	158.3	liq (2)	25.2	24.48	76.4
cyclo- C_6H_{10}	161.7	gas (3)	23.6	24.47	78.0
cyclo- C_6H_{10}	161.7	liq (4)	22.9	24.34	78.7
cyclo- $\text{C}_6\text{H}_{11}\text{CH}=\text{CH}_2$	163.6	liq (1)	24.3	24.63	77.3
$\text{CH}_2=\text{CHCH}_2\text{OH}$	166.5	liq (1)	19.5	24.06	82.1
$\text{CH}_2=\text{CHCOOH}$	182.0	liq (2)	21.3	25.09	80.3
<i>trans</i> -HO ₂ CCH=CHCO ₂ H	184.3	liq (1)	18.8	24.82	82.8
<i>trans</i> -MeO ₂ CCH=CHCO ₂ Me	184.3	liq (1)	18.2	24.72	83.4
cyclo-[C(CO ₂ H)=CH(CH ₂) ₃]	189.1	liq (1)	20.9	25.39	80.7
cyclo-[C(CO ₂ H)=CH(CH ₂) ₄]	184.9	liq (1)	27.3	25.20	76.4
cyclo-[CH=CHCH ₂ CH(CO ₂ H)(CH ₂) ₂]	161.7	liq (1)	21.3	24.05	80.3
$\text{CH}_2=\text{CHCl}$	179.5	gas (1)	19.8	24.79	81.8
$\text{CH}_2=\text{CHF}$	174.3	gas (1)	19.7	24.50	81.9

^a The value in parentheses is the number of determinations.

where D_i and D_f are dissociation energies, h is the Planck constant, L is the Avogadro number, and ν_i and ν_f are the stretching vibration frequencies of bonds i and f , respectively. The second term is the difference between the zero-point energies of the reacting bonds.

2. Activation energy E_e , which includes the zero-point energy of the bond being attacked ($0.5hL\nu_i$) and depends on the experimentally determined activation energy E

$$E_e = E + 0.5(hL\nu_i - RT). \quad (9)$$

3. Distance r_e , which is equal to the sum of the amplitudes of vibrations of the atoms of the reacting bonds in the transition state.

4. Parameters b_i and b_f , which are dynamic characteristics ($2b^2$ is the force constant) of the outgoing bond

$$b_i = \pi\nu_i(2\mu_i)^{1/2}$$

and the incoming bond

$$b_f = \pi\nu_f(2\mu_f)^{1/2},$$

where μ_i and μ_f are the reduced masses of atoms forming the bonds.

The above parameters are related to one another by the following expression:⁴²

$$br_e = \alpha(E_e - \Delta H_e)^{1/2} + E_e^{1/2}. \quad (10)$$

By using the parameter br_e , one can calculate characteristics of a whole group of reactions with $br_e = \text{const}$, for example, the activation energy of the thermally neutral reaction E_{e0} for $\Delta H_e = 0$

$$(E_{e0})^{1/2} = br_e(1 + \alpha)^{-1} \quad (11)$$

and the position of the transition state $r^\ddagger$ in the segment r_e

$$\frac{r^\ddagger}{r_e} = \frac{1}{1 + \alpha}. \quad (12)$$

As a rule, each reaction within one group is characterised by the same pre-exponential factor A (determined in relation to one reaction centre). This allows the activation energy to be expressed in terms of the rate constant k using the Arrhenius equation

$$E = RT \ln \frac{A}{k}. \quad (13)$$

Since for any elementary reaction, $E > 0$, relation (13) holds when $\Delta H_e > \Delta H_{e\min}$, whereas for $\Delta H_e < \Delta H_{e\min}$, the activation energy is very small and amounts to $0.5RT$. In accordance with the parabolic model, $\Delta H_{e\min}$ is related to br_e and α by the expression⁶³

$$\alpha^2 \Delta H_{e\min} = -(br_e)^2 + 2br_e(0.5hL\nu_i)^{1/2} + 0.5hL\nu_i(\alpha^2 - 1). \quad (14)$$

The physical, thermodynamic and kinetic parameters for 15 classes of reactions involving addition of atoms and radicals to carbon—carbon and carbon—oxygen multiple bonds are listed in Table 4.

The parabolic model makes it possible to develop an empirical hierarchy of addition reactions. All the known addition reactions are divided *a priori* into classes in accordance with the atomic structure of the reaction centre in the transition state. Each class is characterised by a pair of force constants of the outgoing and incoming bonds or by the parameters $b = b_i$ and $\alpha = b_i/b_f$ (see above). Subclasses are distinguished in each class. Each subclass is characterised by $r_e = \text{const}$ or $br_e = \text{const}$, which is confirmed by analysis of a large array of experimental results. This fact is illustrated, for example, by the data on the addition of a hydrogen atom to alkenes with various structures (Table 5). For thirty two reactions, $br_e = 24.50 \pm 0.40 \text{ kJ}^{1/2} \text{ mol}^{-1/2}$.

Each subclass of reactions can be described additionally by the energy of the thermally neutral reaction E_{e0} [see Eqn (11)] and by the threshold value $\Delta H_{e\min}$, for which $E = 0.5RT$ provided that

Table 6. Kinetic parameters E_{e0} (kJ mol^{-1}), $b(1 + \alpha)^{-1} \times 10^{-11}$ ($\text{kJ}^{1/2} \text{ mol}^{-1/2} \text{ m}^{-1}$), $r_e \times 10^{11}$ (m), $(r^\ddagger/r_e)_0$ and $-\Delta H_{e\min}$ (kJ mol^{-1}) calculated from Eqns (10)–(12) and (14) for addition reactions of various subclasses.^{44–50}

$X^\cdot$	E_{e0}	$b(1 + \alpha)^{-1} \times 10^{-11}$	$r_e \times 10^{11}$	$(r^\ddagger/r_e)_0$	$-\Delta H_{e\min}$
Reaction $X^\cdot + \text{CH}_2=\text{CHY} \longrightarrow \text{XCH}_2\text{CHY}$					
H $^\cdot$	101.6	2.21	4.56	0.41	211.9
D $^\cdot$	99.6	2.19	4.56	0.41	204.9
Cl $^\cdot$	50.5	1.86	3.82	0.39	82.9
Br $^\cdot$	31.2	1.69	3.30	0.35	37.9
C $^\cdot$ H ₃	82.6	2.45	3.71	0.45	194.4
C ₆ H ₅ $^\cdot$	105.3	2.45	4.19	0.45	252.0
N $^\cdot$ H ₂	61.0	2.24	3.49	0.41	226.0
RO $^\cdot$	65.2	2.23	3.62	0.41	119.0
RO ₂ $^\cdot$	90.5	1.97	4.83	0.36	150.4
R ₃ Si $^\cdot$	76.6	1.78	4.92	0.33	117.5
PhS $^\cdot$	31.4	1.64	3.42	0.30	34.7
Reaction $X^\cdot + \text{HC}\equiv\text{CY} \longrightarrow \text{XCH}=\text{C}^\cdot\text{Y}$					
H $^\cdot$	125.1	2.43	4.60	0.35	229.3
C $^\cdot$ H ₃	97.7	2.72	3.63	0.39	184.7
Reaction $X^\cdot + \text{O}=\text{CR}^1\text{R}^2 \longrightarrow \text{XOC}^\cdot\text{R}^1\text{R}^2$					
H $^\cdot$	102.9	2.30	4.41	0.38	149.7
C $^\cdot$ H ₃	72.9	2.33	3.66	0.39	112.2
R ₃ Si $^\cdot$	114.5	1.70	6.29	0.28	176.8

$\Delta H_e < \Delta H_{e\min}$ [see Eqn (14)]. The kinetic parameters for various subclasses of addition reactions are listed in Table 6. It can be seen that each subclass is characterised by individual values of these parameters. For instance, E_{e0} varies from 31.4 kJ mol^{-1} for the addition of PhS $^\cdot$ to 105.3 kJ mol^{-1} for the addition of the phenyl radical to an alkene double bond.

VI. The contribution of enthalpy of an addition reaction to its activation energy

The parabolic model postulates a non-linear relationship between the activation energy and the enthalpy of a reaction [see Eqn (10)]. The contribution of enthalpy to the activation energy ΔE_H can be estimated as the difference $\Delta E_H = E_e - E_{e0}$.

Transformation of Eqn (10) gives the following equation for ΔE_H as a function of ΔH_e ⁴²

$$\Delta E_H = \frac{2\alpha(br_e)^2}{\alpha^2 - 1} \left\{ \left[\frac{\Delta H_e(\alpha^2 - 1)}{(br_e)^2} - 1 \right]^{1/2} - 1 \right\} + \frac{\alpha^2 \Delta H_e^2}{\alpha^2 - 1}. \quad (15)$$

When the range of variation of ΔH_e is narrow, this dependence is close to linear

$$\Delta E_H = \frac{\alpha}{1 + \alpha} \Delta H_e + \frac{\alpha}{4(br_e)^2} \Delta H_e^2. \quad (16)$$

In a review,⁴² the E_{e0} values calculated from experimental br_e parameters made it possible to evaluate correctly the contribution of the enthalpy of addition to its activation energy. As an example, Table 7 presents the results of this comparison for two groups of addition reactions.

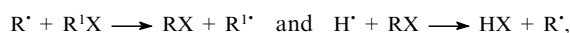
It can be seen that these reactions are highly exothermic and the contribution of enthalpy to the activation energy is fairly high; it varies from -43.6 to $-98.7 \text{ kJ mol}^{-1}$, *i.e.* amounts to 40%–50% of ΔH .

Table 7. Contribution of the reaction enthalpy ΔH to the activation energy ΔE_H .

R	Y	$-\Delta H/$ kJ mol $^{-1}$	$E_e/$ kJ mol $^{-1}$	$-\Delta E_H/$ kJ mol $^{-1}$
Reaction $H^\bullet + CH_2=CRY \longrightarrow CH_3C^\bullet RY$ (see Ref. 44)				
H	H	162.1	22.5	79.1
H	Me	165.3	21.0	80.6
Me	Me	173.3	18.0	83.6
H	Cl	179.5	19.8	81.8
H	Ph	204.1	19.2	93.0
Ph	Ph	213.3	19.0	98.7
Reaction $CH_3^\bullet + CH_2=CRY \longrightarrow C_2H_5C^\bullet RY$ (see Ref. 46)				
H	H	98.5	39.0	43.6
H	Me	96.1	36.9	45.7
Me	Me	98.3	35.7	46.9
H	Cl	104.3	33.6	49.0
H	Ph	143.3	26.6	63.4
Ph	Ph	154.0	24.5	69.3

VII. Force constants of reacting bonds

The activation energy of a thermally neutral reaction is determined by two parameters — the distance r_e and the force constants of the reacting bonds α and b . In some classes of radical abstraction reactions, namely in those presented below,



only the force constants change on passing from one class to another; thus, only the parameters α and b determine the activation energy of a thermally neutral reaction.⁸⁰ There are no such examples among addition reactions; therefore, it is expedient to compare different classes of reactions assuming (conditionally) that $r_e = \text{const}$. The parameter r_e for each reaction was taken to be 3.713×10^{-11} m, as for the addition of the methyl radical to $CH_2=CRY$, while the parameters b_i and b_f were varied in conformity with the structure of the reaction centre. The calculations were carried out using Eqn (11).

Reaction	E_{e0} (calculated)/ kJ mol $^{-1}$	E_{e0} (exp)/ kJ mol $^{-1}$
$H^\bullet + C=C$	67.3	101.6
$H^\bullet + O=C$	73.2	102.9
$H^\bullet + C \equiv C$	81.3	125.2
$Me^\bullet + C=C$	82.6	82.6
$Me^\bullet + O=C$	74.9	68.1
$Me^\bullet + C \equiv C$	64.0	97.7

Comparison of the calculated and experimental E_{e0} values shows a substantial influence of, on the one hand, the force constants (the range of variation of E_{e0} is 64–83 kJ mol $^{-1}$) and, on the other hand, the parameter r_e [E_{e0} (calculated) $\neq E_{e0}$ (exp)].

VIII. Triplet repulsion in addition reactions

The activation energy of radical abstraction is influenced by the so-called triplet repulsion in the transition state.^{40, 42} This influence is manifested in the fact that the stronger the $X-R$ bond towards which the hydrogen atom moves in the thermally neutral reaction $X^\bullet + RH$, the higher the activation energy of this reaction. The triplet repulsion is due to the fact that three electrons cannot be accommodated in the bonding orbital of $X-C$; therefore, one electron occupies the non-bonding $X-C$ orbital. Meanwhile, the stronger the $X-C$ bond, the higher the energy of the non-bonding orbital and the higher the activation energy of abstraction.

How do matters stand with radical addition? Comparison of E_{e0} and r_e with the energy of dissociation of the resulting bond D_e has shown that this influence certainly does exist.^{44, 46, 48} The parameters E_{e0} and r_e are juxtaposed with the dissociation energy of the bond formed $D_e(X-C)$ in Table 8 and in Fig. 3. For reactions of one class, namely, $X^\bullet + CH_2=CHY$, the linear correlation $E_{e0} = \text{const} [D_e(X-C)]^2$ holds; $\text{const} = 5.95 \times 10^4$ mol kJ $^{-1}$. The following correlation was found to be fulfilled for reactions of all the thirteen classes considered:

$$r_e = a D_e(X-C), \quad (17)$$

where $a = (1.01 \pm 0.03) \times 10^{-13}$ for the addition of atoms and $a = (0.98 \pm 0.02) \times 10^{-13}$ m mol kJ $^{-1}$ for the addition of radicals (see Fig. 3). This correlation should be regarded as an empirical proof of the fact that the non-bonding orbital of the bond being

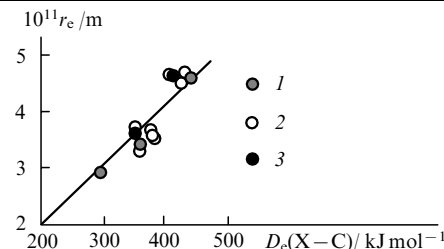


Figure 3. Correlation of the parameter r_e (parabolic model) with the strength $D_e(X-C)$ of the bond formed upon atom and radical addition to the $C=C$ and $C \equiv C$ multiple bonds;⁴⁷ (1) atom + $C=C$, (2) $X' + C=C$ or $C \equiv C$, (3) $H'(R') + O=C$.

Table 8. Parameters of various classes of radical addition and the strengths $D_e(X-C)$ of the bonds formed.^{44–50}

Reaction	$E_{e0}/$ kJ mol $^{-1}$	$r_e \times 10^{11} /$ m	$D_e(X-C)/$ kJ mol $^{-1}$	$\frac{r_e}{D_e(X-C)} \times 10^{13} /$ m mol kJ $^{-1}$
$H^\bullet + CH_2=CHY \longrightarrow CH_3C^\bullet HY$	101.6	4.563	439	1.04
$D^\bullet + CH_2=CHY \longrightarrow DCH_2C^\bullet HY$	99.6	4.557	439	1.04
$Cl^\bullet + CH_2=CHY \longrightarrow ClCH_2C^\bullet HY$	50.5	3.427	357	0.96
$Br^\bullet + CH_2=CHY \longrightarrow BrCH_2C^\bullet HY$	31.2	2.949	299	0.99
$H^\bullet + CH \equiv CY \longrightarrow CH_2=C^\bullet Y$	125.2	4.608	462	1.00
$H^\bullet + O=CR^1R^2 \longrightarrow HOC^\bullet R^1R^2$	102.9	4.402	459	0.96
$C^\bullet H_3 + CH_2=CHY \longrightarrow C_2H_5C^\bullet HY$	82.6	3.713	378	0.98
$Me_2C^\bullet H + CH_2=CHY \longrightarrow Me_2CHCH_2C^\bullet HY$	78.3	3.617	372	0.97
$Me_3C^\bullet + CH_2=CHY \longrightarrow Me_3CCH_2C^\bullet HY$	68.3	3.377	360	0.94
$C_6H_5^\bullet + CH_2=CHY \longrightarrow C_6H_5CH_2C^\bullet HY$	105.3	4.194	436	0.96
$N^\bullet H_2 + CH_2=CHY \longrightarrow NH_2CH_2C^\bullet HY$	62.1	3.53	360	0.98
$RO^\bullet + CH_2=CHY \longrightarrow ROCH_2C^\bullet HY$	65.2	3.617	359	1.01
$R^\bullet + O=CR^1R^2 \longrightarrow ROC^\bullet R^1R^2$	68.1	3.540	365	0.97

formed actually does participate in the generation of the activation energy of addition. The stronger this bond, the higher the energy of the non-bonding orbital and the higher the activation energy. Empirical correlation (17) can be used to estimate roughly the activation energies of diverse addition reactions.

IX. The influence of neighbouring π bonds on the activation energy of radical addition

Radical abstraction reactions that involve molecules with π bonds in the vicinity of the reaction centre are characterised by higher E_{e0} values than the corresponding reactions involving similar hydrocarbons without these bonds. This is due to triplet repulsion.^{41,42} In these reactions, the three electrons of the reaction centre interact with the neighbouring π electrons; as a consequence, the energy of the non-bonding orbital in the transition state increases and, hence, the activation energy also increases. Do neighbouring π bonds influence the E_{e0} values of radical addition? In order to answer this question, let us compare the br_e and E_{e0} parameters for the addition of $H^\bullet$, $C^\bullet H_3$, $RO^\bullet$, $RO_2^\bullet$, and $R_3Si^\bullet$ to the monomers $CH_2=CHY$ and monomers with double bonds in the α -position relative to the double bond being attacked. If the monomer contains an aromatic ring or a double bond in the α -position, the activation energy of a thermally neutral reaction increases; if there are two aromatic rings in the α -position, E_{e0} increases to even a greater extent (Table 9). The difference between $E_{e0}(\pi)$ and $E_{e0}(CH_2=CHY)$ can be used to estimate the contribution of this factor to the activation barrier⁴¹

$$\Delta E(\pi) = \Delta E_{e0}(\pi) - E_{e0}(CH_2=CHY). \quad (18)$$

Triplet repulsion also manifests itself in the reactions in question; for example, in the reaction

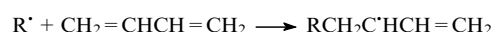


Table 9. Influence of a π bond adjacent to the reaction centre on the activation energy of the radical addition to alkenes.^{44–50}

Reaction	br_e^a	E_{e0}^b	ΔE_π^b	$\Delta D_e(\pi)^c$
$H^\bullet + CH_2=CHY$	24.59	101.6	0	0
$H^\bullet + CH_2=CHPh$	25.85	112.2	10.6	24.1
$H^\bullet + CH_2=CPh_2$	26.47	117.7	16.1	36.0
$H^\bullet + \text{cyclo-}\Delta^{1,3}\text{-C}_6\text{H}_8$	26.47	117.7	16.1	36.0
$H^\bullet + CH_2=CHCN$	25.45	108.8	7.2	16.4
$C^\bullet H_3 + CH_2=CHR$	20.01	82.6	0	0
$C^\bullet H_3 + CH_2=CHPh$	20.82	89.4	6.8	15.5
$C^\bullet H_3 + CH_2=CMePh$	20.67	88.7	6.1	12.6
$C^\bullet H_3 + CH_2=CPh_2$	21.33	94.4	11.8	25.2
$C^\bullet H_3 + CH_2=CHCH=CH_2$	20.88	89.9	7.3	16.6
$C^\bullet H_3 + MeCH=CHCH=CHMe$	21.15	92.2	9.6	21.8
$C^\bullet H_3 + CH_2=CMeCMe=CH_2$	21.03	91.2	8.6	19.5
$C^\bullet H_3 + \text{cyclo-}\Delta^{1,3}\text{-C}_6\text{H}_8$	22.27	102.3	19.7	43.2
$C^\bullet H_3 + \text{cyclo-}\Delta^{1,4}\text{-C}_6\text{H}_8$	22.23	101.9	19.3	42.5
$N^\bullet H_2 + CH_2=CHR$	18.82	61.0	0	0
$N^\bullet H_2 + (E)\text{-CH}_2=CHCH=CH_2$	20.52	72.5	10.4	23.7
$RO^\bullet + CH_2=CHR$	19.49	61.8	0	0
$RO^\bullet + CH_2=CHPh$	21.09	76.4	14.6	30.6
$RO_2^\bullet + CH_2=CHR$	26.04	90.5	0	0
$RO_2^\bullet + CH_2=CHPh$	27.23	99.0	8.5	22.8
$RO_2^\bullet + CH_2=CPh_2$	28.04	105.0	14.5	38.3
$R_3Si^\bullet + CH_2=CHR$	26.46	76.6	0	0
$R_3Si^\bullet + CH_2=CHPh$	28.52	89.0	12.4	27.9
$R_3Si^\bullet + O=CR^1R^2$	37.62	114.5	0	0
$R_3Si^\bullet + O=CMePh$	39.74	127.6	13.1	22.5
$R_3Si^\bullet + O=CPh_2$	40.02	129.3	14.8	25.5

^a Expressed in $\text{kJ}^{1/2} \text{mol}^{-1/2}$; ^b expressed in kJ mol^{-1} ; ^c $\Delta D_e(\pi)$ is the energy of triplet repulsion, kJ mol^{-1} .

a multicentre multielectron $R\cdots C\cdots C\cdots C$ bond arises in the transition state; this increases the strength of the bond, and, hence, enhances the triplet repulsion and its contribution to the activation energy. It can be seen from the data of Table 9 that this contribution can reach 20 kJ mol^{-1} . The increase in the dissociation energy $D_e(X-C)$ caused by this electron delocalisation can be estimated using relation (18).

The same trend is observed for the addition of the benzyl radical to the monomers $CH_2=CRY$ (see Table 10).⁴⁸ The average br_e and E_{e0} values for these reactions are $24.91 \pm 0.49 \text{ kJ}^{1/2} \text{mol}^{-1/2}$ and $128.0 \text{ kJ mol}^{-1}$, respectively; the values for the addition of methyl radical are $19.93 \pm 0.4 \text{ kJ}^{1/2} \text{mol}^{-1/2}$ and 82.6 kJ mol^{-1} . The greater E_{e0} value found in the case of the addition of benzyl radicals points to stronger triplet repulsion caused by electron delocalisation.

Table 10. Parameters br_e and E_{e0} for the addition of benzyl radicals to monomers $CH_2=CRY$.

R	Y	$br_e/\text{kJ}^{1/2} \text{mol}^{-1/2}$	$E_{e0}/\text{kJ mol}^{-1}$
Me	OMe	24.98	128.7
H	OEt	24.85	127.4
H	Ph	24.88	127.7
Me	Ph	24.93	128.2

The substantial influence of the π bonds located near the reaction centre on the activation energy can also be followed for the addition of methyl radicals to the $C=O$ group in *p*-benzoquinone. This can be clearly seen when comparing the corresponding parameters for the addition of a methyl radical to acetone and to *p*-benzoquinone.⁴⁹

R^1COR^2	$br_e/\text{kJ}^{1/2} \text{mol}^{-1/2}$	$E_{e0}/\text{kJ mol}^{-1}$	$10^{11}r_e/\text{m}$
Me_2CO	21.95	68.1	3.54
OC_6H_4O	23.15	81.1	3.86

The observed difference in the parameters is due most likely to the electron delocalisation in the aromatic ring and, hence, to the increase in the triplet repulsion. The difference between the E_{e0} values for the reactions considered amounts to 13 kJ mol^{-1} . For the addition of polystyrene radical to *p*-benzoquinone, $br_e = 25.03 \text{ kJ}^{1/2} \text{mol}^{-1/2}$ and $E_{e0} = 94.8 \text{ kJ mol}^{-1}$. In this case, the E_{e0} value is 26.7 kJ mol^{-1} greater than that for the reaction of the methyl radical with acetone. The very large $\Delta E(\pi)$ value can be accounted for by the interaction of the π electrons of the two neighbouring benzene rings with the reaction centre.

The addition of peroxy radicals to alkenes deserves special discussion. This class of reaction is characterised by the parameter $br_e = 26.04 \text{ kJ}^{1/2} \text{mol}^{-1/2}$ (see Ref. 45). Estimation of this parameter from relation (17) gives $br_e = 16.26 \text{ kJ}^{1/2} \text{mol}^{-1/2}$, which is much lower than the experimental value. One reason for this discrepancy, as in the case of reactions subject to the influence of π bonds, is as follows. In the $RO\cdots O\cdots C\cdots C$ transition state, the *p* electrons of the two oxygen atoms interact with the electrons of the atoms of the reaction centre; this increases the triplet repulsion and E_{e0} .

With allowance for the examples considered above, correlation (17) can be extended and written in the following form:

$$r_e = a[D_e + \Delta D_e(\pi)], \quad (19)$$

where $\Delta D_e(\pi)$ is the increase in the energy of the non-bonding orbital caused by delocalisation of the neighbouring π or *p* electrons. The $\Delta D_e(\pi)$ values are listed in Table 9.

X. The role of the radius of the atom carrying the free valence

The greater the radius of the atom carrying the free valence, the higher the E_{e0} for radical abstraction.⁴² Does the radius of the atom which attacks the double bond influence the activation energy of addition reactions? This question was answered as a result of analysis of experimental data on the addition of triethylsilyl and phenylthiyl radicals to alkenes.⁵⁰

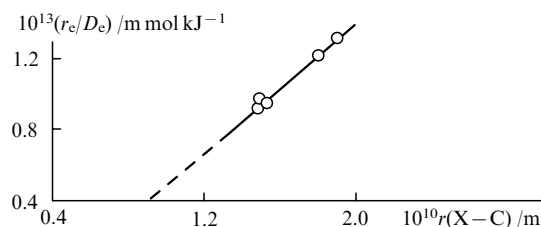


Figure 4. Correlation between the ratio of the parameters r_e/D_e (parabolic model) and the length $r(X-C)$ of the incoming bond for the addition of the $R^\bullet$, $N^\bullet H_2$, $RO^\bullet$, $RS^\bullet$, and $R_3Si^\bullet$ radicals to alkenes (see also Table 11).⁵⁰

Since the strength of the $C-X$ (D_e) bond being formed influences the parameter r_e [see Eqn (17)], the characteristic to be compared for the addition of various radicals to alkenes is the r_e/D_e ratio (Table 11, Fig. 4). The lengths $r(C-X)$ of the bonds formed upon the addition of radicals such as $C^\bullet H_3$, $N^\bullet H_2$ and $RO^\bullet$ to the $C=C$ bond and upon the addition of $C^\bullet H_3$ to the $C=O$ bond are close; therefore, the ratio $r_e/D_e = \text{const}$. However, in the case of addition of $PhS^\bullet$ and $R_3Si^\bullet$ to the $C=C$ bond, the r_e/D_e ratio is much greater and a linear correlation is observed between r_e/D_e and $r(C-X)$. The correlation has the following form⁵⁰

Table 11. Strengths (D_e /kJ mol⁻¹) and lengths [$r(C-X)$ or $r(X-O)$ /m] of the bonds formed upon the addition of $X^\bullet$ radicals to $C=C$ or $C=O$ double bonds.⁵⁰

$X^\bullet$	D_e	$10^{10}r(C-X)$ or $10^{10}r(O-X)$	$10^{11}r_e/m$	$10^{13}(r_e/D_e)/$ m mol kJ ⁻¹
$X^\bullet + CH_2=CHY \longrightarrow XCH_2CHY$				
$C^\bullet H_3$	378	1.52	3.71	0.98
$N^\bullet H_2$	360	1.47	3.53	0.98
$RO^\bullet$	359	1.43	3.62	1.01
$RS^\bullet$	284	1.79	3.41	1.20
$R_3Si^\bullet$	378	1.89	4.91	1.30
$X^\bullet + O=CR^1R^2 \longrightarrow XOC^*R^1R^2$				
$C^\bullet H_3$	365	1.43	3.54	0.97
$R_3Si^\bullet$	487	1.64	6.28	1.29

Table 12. Contribution of the polar effect (ΔE_μ /kJ mol⁻¹) to the activation energy of the addition of polar radicals to polar monomers $CH_2=CRY$ (calculated from the data of several studies^{45,46,48,81-83}).

$CH_2=CRY$	$Me_2(HO)C^\bullet$	$Me_2(CN)C^\bullet$	$Me_3COC(O)C^\bullet H_2$	$sec-RO_2^\bullet$	$tert-RO_2^\bullet$	$HO_2^\bullet$
$CH_2=CHOEt$	-1.9	-4.9	13.2	—	—	—
$CH_2=CMeOMe$	-6.5	-9.4	10.1	—	—	—
$CH_2=CHOAc$	-15.1	-11.2	17.5	9.5	7.3	11.5
$CH_2=CMeOAc$	-16.4	-4.3	19.5	—	—	—
$CH_2=CClMe$	-8.2	-4.4	10.8	—	—	—
$CH_2=CCl_2$	-10.2	-3.8	13.4	—	—	—
$CH_2=CHCOOMe$	-20.1	-1.4	13.1	-0.3	-2.0	—
$CH_2=CMeCOOMe$	—	-3.4	—	-5.2	-6.4	-4.7
$CH_2=CHCN$	-23.2	-0.9	13.8	-9.0	-10.8	-7.9

$$r_e = \frac{(1 + \alpha)}{b} E_{e0}^{1/2} = 8.81 \times 10^4 [r(C-X) - 0.42 \times 10^{-10}] D_e. \quad (20)$$

Thus, the radius of the atom carrying the free valence has a substantial influence on the activation barrier to the addition reaction — the greater the radius of this atom, the higher the activation energy. Apparently, this effect is due to repulsion in the transition state, the repulsion being due to the interaction between the electron shells of the double bond being attacked and the atom which attacks this bond.

XI. Interaction of two polar groups

The polar effect involved in radical addition has been repeatedly discussed in the scientific literature.^{3,6,19-25} The parabolic model opens up new prospects for the correct estimation of the polar effect. It permits one to determine the contribution of this effect to the activation energy. This contribution (ΔE_μ) is estimated by choosing a reference reaction which involves the same reaction centre but in which one or both reactants are non-polar. The reference reaction is characterised by the parameter br_e and the reaction with two polar reactants is characterised by the parameter $(br_e)_\mu$. The component of the activation energy caused by polar interaction (ΔE_μ) is calculated from the equation⁴²

$$\Delta E_\mu = [(br_e)_\mu^2 - (br_e)^2](1 + \alpha)^{-2}. \quad (21)$$

Table 12 presents the results of calculation of ΔE_μ for the reactions of six polar radicals with a number of polar monomers.^{45,46,81-83} It can be seen that the polar interaction in the transition states for the addition can either decrease ($\Delta E_\mu < 0$) or, in other cases, increase ($\Delta E_\mu > 0$) the activation energy. The ΔE_μ values vary from +19.5 to -23 kJ mol⁻¹, i.e. they can be rather large.

XII. Multidipole interaction in addition reactions

The multidipole interaction in a bimolecular reaction arises if one or both reactants contain several polar groups.⁸⁴ The multidipole effect shows itself as a deviation of the rate constant for the addition of a polar radical to a polyfunctional compound (calculated in relation to one reaction centre) from the rate constant for the addition to a monofunctional compound. The multidipole effect was discovered for radical abstraction of a hydrogen atom from polyfunctional esters induced by peroxy radicals.⁸⁴ Later, this effect has also been found in the addition of peroxy radicals to the double bonds of polyatomic unsaturated esters.⁸⁵ Table 13 summarises the results of calculations of the contribution of the multidipole effect to the activation energy performed using relation (21). A monofunctional ester of the corresponding structure served as the reference compound. It can be seen that the role of the multidipole interaction in these reactions is fairly low: the contribution of the interaction of several polar groups $\Delta \Delta E_\mu$ varies from 0.8 to 2.3 kJ mol⁻¹.

Table 13. Multidipole effect in the addition of cumeneperoxy radicals to unsaturated polyatomic esters (n is the number of reacting double bonds in the ester molecule).⁸⁵

Ester	k (323 K) ^a	k/n ^a	$\Delta\Delta E_{\mu}$ ^b
$\text{CH}_2 = \text{CHCO}_2\text{Me}$	0.50	0.50	0
$(\text{CH}_2 = \text{CHCO}_2\text{CH}_2)_2\text{CMe}_2$	0.76	0.38	0.8
$(\text{CH}_2 = \text{CHCO}_2\text{CH}_2)_2\text{CHOCOCH} = \text{CH}_2$	1.05	0.35	1.0
$(\text{CH}_2 = \text{CHCO}_2\text{CH}_2)_4\text{C}$	1.28	0.32	1.2
$\text{CH}_2 = \text{CMeCO}_2\text{Me}$	1.79	1.79	0
$(\text{CH}_2 = \text{CMeCO}_2\text{CH}_2)_2\text{CHOCOMeC} = \text{CH}_2$	3.93	1.31	0.9
$(\text{CH}_2 = \text{CMeCO}_2\text{CH}_2)_4\text{C}$	3.08	0.77	2.3

^a Expressed in litre $\text{mol}^{-1} \text{s}^{-1}$. ^b Expressed in kJ mol^{-1} .

The multidipole effect is also manifested in the addition of chlorine atoms to chloroalkenes. The scope of influence of this factor on the activation energy of these reactions can be judged from the data given in Table 14.

Table 14. Parameters br_e , ΔE_{μ} and $\Delta\Delta E_{\mu}$ for the addition of chloride to chloroalkenes.⁴⁴

Alkene	$br_e / \text{kJ}^{1/2} \text{mol}^{-1/2}$	$\Delta E_{\mu} / \text{kJ mol}^{-1}$	$-\Delta\Delta E_{\mu} / \text{kJ mol}^{-1}$
$\text{CH}_2 = \text{CHCl}$	21.23	17.0	0.0
<i>cis</i> - $\text{CHCl} = \text{CHCl}$	20.43	11.4	5.6
$\text{CH}_2 = \text{CCl}_2$	19.64	6.6	10.4
$\text{CHCl} = \text{CCl}_2$	20.50	11.8	5.2
$\text{CCl}_2 = \text{CCl}_2$	19.46	5.6	11.4

The interaction of a polar reaction centre with one polar C—Cl group increases the activation energy by 17 kJ mol^{-1} , whereas the interaction with several polar C—Cl groups, conversely, results in a lower activation energy.

XIII. Steric hindrance

The addition of trialkylsilyl radicals to 1,2-disubstituted ethylene derivatives is subject to a steric effect. This shows itself in the E_{e0} value for the $\text{Et}_3\text{Si}^\bullet$ addition to $\text{RCH} = \text{CHR}$ being greater than that for the addition of the same radical to $\text{CH}_2 = \text{CHR}$.⁵⁰ The contribution of steric repulsion to the activation energy can be characterised by the increment ΔE_s .

Alkene	$br_e / \text{kJ}^{1/2} \text{mol}^{-1/2}$	$E_{e0} / \text{kJ mol}^{-1}$	$\Delta E_s / \text{kJ mol}^{-1}$
$\text{CH}_2 = \text{CHR}$	26.46	76.6	0.0
$\text{RCH} = \text{CHR}$	27.54	83.0	6.4 ± 0.7

Table 15. Thermodynamic (ΔH , D_e in kJ mol^{-1}) and kinetic (α and E , E_{e0} in kJ mol^{-1}) parameters for the addition of radicals to the carbon and oxygen atoms of the carbonyl group.⁵¹

Reaction	α	ΔH	D_e	E	E_{e0}
$\text{H}^\bullet + \text{Me}_2\text{CO} \longrightarrow \text{Me}_2\text{CHO}^\bullet$	1.601	−53.3	406.5	39.8	82.5
$\text{H}^\bullet + \text{Me}_2\text{CO} \longrightarrow \text{Me}_2\text{C}^\bullet\text{OH}$	1.274	−102.2	459.7	41.8	138.0
$\text{Me}^\bullet + \text{Me}_2\text{CO} \longrightarrow \text{Me}_3\text{CO}^\bullet$	1.336	−34.0	366.4	56.5	83.1
$\text{Me}^\bullet + \text{Me}_2\text{CO} \longrightarrow \text{Me}_2\text{C}^\bullet\text{OMe}$	1.570	−21.3	353.1	44.2	63.7
$\text{Me}^\bullet + \text{PhCOMe} \longrightarrow \text{PhMe}_2\text{CO}^\bullet$	1.336	−14.2	333.8	64.3	69.0
$\text{Me}^\bullet + \text{PhCOMe} \longrightarrow \text{PhMeC}^\bullet\text{OMe}$	1.570	−44.2	348.6	41.2	62.1
$\text{HO}^\bullet + \text{Me}_2\text{CO} \longrightarrow \text{Me}_2\text{C}(\text{OH})\text{O}^\bullet$	1.645	−81.2	424.0	35.7	88.8
$\text{HO}^\bullet + \text{Me}_2\text{CO} \longrightarrow \text{Me}_2\text{C}^\bullet\text{O}_2\text{H}$	1.850	165.0	171.1	171.4	12.2
$\text{MeO}^\bullet + \text{Me}_2\text{CO} \longrightarrow \text{Me}_2(\text{MeO})\text{CO}^\bullet$	1.570	−37.2	379.6	46.6	75.2
$\text{MeO}^\bullet + \text{Me}_2\text{CO} \longrightarrow \text{Me}_2\text{C}^\bullet\text{O}_2\text{Me}$	1.850	157.6	164.1	164.0	11.2
$\text{Me}^\bullet + \text{Me}_2\text{CO} \longrightarrow \text{Me}_2(\text{MeOO})\text{CO}^\bullet$	1.931	48.8	290.0	60.0	33.7

No effect of this type is manifested for the addition of alkyl radicals to the same alkenes.⁴⁶ Evidently, the steric effect involved in the addition of trialkylsilyl radicals to 1,2-disubstituted ethylene derivatives is due to the repulsion between the carbon and silicon atoms, caused by the large size of the silicon atom, in the reaction centre of the transition state.

The addition of tris(*tert*-butyl)phenoxyl radical to styrene can serve as an example of reaction subject to the steric effect. This reaction is characterised by $br_e = 23.89 \text{ kJ}^{1/2} \text{mol}^{-1/2}$ (see Ref. 49), whereas the addition of the *tert*-butoxyl radical to styrene (a reaction with a similar structure of the reaction centre) has the parameter $br_e = 21.09 \text{ kJ}^{1/2} \text{mol}^{-1/2}$ (see Ref. 49). The difference between these values is matched by the difference between the activation energies of the corresponding thermally neutral reactions, $\Delta E_{e0} = 21.6 \text{ kJ mol}^{-1}$; this can be regarded as a rough estimate of the energy of additional repulsion in the transition state of the reacting system. This repulsion in the transition state is brought about by two *tert*-butyl groups of the phenoxyl radical.

XIV. Competition between the addition of free radicals to the carbon and oxygen atoms of the carbonyl group

The reaction enthalpy and the triplet repulsion are two factors influencing appreciably the activation energy of addition. The triplet repulsion in the addition of atoms and radicals to the C=C bonds attached to the CH_2 and CHY groups does not differ much because the D_e values for these processes are close (see Section VIII). The difference between the reactivities of the CH_2 and CHY groups is determined by the energy of stabilisation of the radicals formed and thus by the reaction enthalpy.

A different situation is observed for the addition of radicals to C=O bonds. In this case, triplet repulsion which accompanies the addition of the $\text{X}^\bullet$ radical to carbon differs substantially from that involved in the addition to oxygen because of the different strengths of the resulting bonds, C—X and X—O. For example, the dissociation energies in ethanol are $D_e(\text{C—H}) = 417 \text{ kJ mol}^{-1}$ and $D_e(\text{O—H}) = 458 \text{ kJ mol}^{-1}$. Therefore, the ratio of the activation energies E_{e0} of the corresponding thermally neutral addition reactions, which is proportional to the $D_e^2(\text{C—H})/D_e^2(\text{O—H})$ ratio, is equal to 0.83 [see Eqns (11)–(17)]. Thus, two factors compete in the addition of atoms and radicals to a carbonyl group, namely, the enthalpy of the reaction and the triplet repulsion, which both influence the activation energy. The problem of competition between the addition of atoms and radicals to either carbon or oxygen atom of the carbonyl group has been considered in the literature.⁵¹ The thermodynamic and kinetic parameters of such addition are presented in Table 15. Analysis of the ΔH , E , and E_{e0} values leads to the following conclusions.

1. Hydrogen atoms add both to oxygen and to carbon, the corresponding rate constants being close (the difference between the activation energies is only 2 kJ mol^{-1}). This is due to the fact that the influence of the reaction enthalpy (see the ΔH values) is counterbalanced by the effect of triplet repulsion, which is higher for the hydrogen addition to oxygen: $\Delta H(\text{O}) - \Delta H(\text{C}) = -48.9 \text{ kJ mol}^{-1}$ but $E_{\text{e0}}(\text{C}) < E_{\text{e0}}(\text{O})$ and $\Delta E_{\text{e0}} = 55.5 \text{ kJ mol}^{-1}$. In this reaction, the thermodynamic (ΔE_H) and kinetic (E_{e0}) factors act in the opposite directions and cancel out each other.

2. When a methyl radical adds to the carbonyl group of acetone, the heat of the addition to carbon is greater than the heat of the addition to oxygen: $[\Delta H(\text{C}) - \Delta H(\text{O})] = -12.7 \text{ kJ mol}^{-1}$. However, due to the higher triplet repulsion [$E_{\text{e0}}(\text{C}) > E_{\text{e0}}(\text{O})$], the activation energy for the addition of the methyl radical to carbon is higher than that for its addition to oxygen [the difference between the activation energies $E(\text{C}) - E(\text{O}) = +12.3 \text{ kJ mol}^{-1}$]. In this case, triplet repulsion has the predominant influence on the energy. As a consequence, the more exothermic reaction has a higher activation energy.

3. In the addition of a methyl radical to the carbonyl group of acetophenone, both factors (thermodynamic and kinetic) act in the same direction (compare the ΔH and E_{e0}); therefore, the predominant pathway is the addition of the methyl radical to the oxygen atom, giving rise to a more stable benzyl radical: $\Delta E = E(\text{O}) - E(\text{C}) = 23 \text{ kJ mol}^{-1}$.

4. Hydroxyl and alkoxyl radicals add only to the carbon atom because this addition is exothermic, whereas the addition to oxygen is endothermic.

5. The addition of a peroxy radical to the carbonyl group is an endothermic reaction; the very high activation energy (60.0 kJ mol^{-1}) makes this process virtually impossible because the addition product would rapidly decompose to the starting compounds (see Section II).

XV. Comparison of radical addition and radical abstraction reactions

In a previous study,⁴¹ diverse reactions of radical abstraction have been analysed in terms of the parabolic model and ten structural and thermodynamic factors determining the activation energy of these reactions have been established. In this study, we distinguish factors which influence the activation energy of radical addition. Since both addition and abstraction reactions are analysed in terms of the same (parabolic) model, it is possible to compare these two absolutely different types of reactions regarding the character and the degree of influence of each factor on the activation energy.

Table 16 lists the factors that influence the activation barriers to both radical abstraction and addition. It can be seen that the factors having a positive influence on the activation energy of abstraction and addition include the reaction enthalpy, the force

Table 16. Factors influencing the activation energy of radical abstraction and addition.

Factor influencing the activation energy	Radical abstraction	Radical addition
Enthalpy	+	+
Force constants of the reacting bonds	+	+
Strength of the incoming bond	+	+
The presence of π -bonded groups	+	+
Different electronegativities of atoms in the reaction centre	—	no effect
Radius of the atom carrying a free valence	+	+
The presence of polar groups	$\pm$	$\pm$
Steric effect	+	+

Note. ‘Plus’ stands for an increase and ‘minus’ means a decrease in E due to the influence of this factor.

constants of the reacting bonds, the strength of the bond being formed, the radius of the attacking atom, and π bonds or bulky substituents present in the vicinity of the reaction centre. Polar groups (one or several) in the reactant molecules either increase or decrease the activation energy.

The difference between the abstraction and addition reactions is as follows. First, they differ in the geometry of the reaction centre. In the case of abstraction, the reaction centre is linear — all three atoms are aligned and this geometry ensures the minimum activation barrier. In the case of addition, since the molecular orbital of the π -C—C bond is arranged at an angle of 90° in relation to the line connecting the atoms, the reaction centre is a triangle (the three atoms X—C—C of the reaction centre are located at the vertices of a triangle with an X—C—C angle of 109° , see Fig. 1). Naturally, this distinction exerts an effect on the activation energy of addition. Second, the activation energy of abstraction is affected by the difference between the electronegativities of the atoms of the reaction centre, namely, the greater this difference, the lower the activation energy. No influence of this type has been noted in addition reactions.

It is pertinent to compare the activation parameters for various classes of addition reactions with the corresponding parameters of radical abstraction.⁴² The results of this comparison for five parameters and six subclasses of abstraction and addition are summarised in Table 17. The abstraction of a hydrogen atom in a thermally neutral reaction always proceeds more easily than the addition of a hydrogen atom to a double bond (see the E_{e0} values). This is due to the different geometries of the reaction centre in these reactions and to higher repulsion in the non-linear reaction centre. An important role is played by the

Table 17. Kinetic parameters of radical abstraction and addition.^{42, 44, 46, 52, 53}

Reaction	$E_{\text{e0}}/\text{kJ mol}^{-1}$	$10^{11}r_{\text{e}}/\text{m}$	dE/dH	$(r^{\neq}/r_{\text{e}})_0$	$\Delta H_{\text{e min}}/\text{kJ mol}^{-1}$
$\text{H}^{\cdot} + \text{RH} \longrightarrow \text{H}_2 + \text{R}^{\cdot}$	54.6	3.762	0.48	0.48	94.5
$\text{H}^{\cdot} + \text{CH}_2=\text{CHX} \longrightarrow \text{CH}_3\text{C}^{\cdot}\text{HX}$	101.6	4.563	0.59	0.41	227.6
$\text{R}^{\cdot} + \text{R}^1\text{H} \longrightarrow \text{RH} + \text{R}^{1\cdot}$	74.0	4.595	0.50	0.50	153.1
$\text{C}^{\cdot}\text{H}_3 + \text{CH}_2=\text{CHX} \longrightarrow \text{CH}_3\text{CH}_2\text{C}^{\cdot}\text{HX}$	82.6	3.713	0.54	0.45	194.4
$\text{RO}^{\cdot} + \text{RH} \longrightarrow \text{ROH} + \text{R}^{\cdot}$	55.4	3.572	0.44	0.56	99.7
$\text{RO}^{\cdot} + \text{CH}_2=\text{CHX} \longrightarrow \text{ROCH}_2\text{C}^{\cdot}\text{HX}$	65.2	3.617	0.58	0.41	119.0
$\text{RO}_2^{\cdot} + \text{R}^1\text{H} \longrightarrow \text{ROOH} + \text{R}^{1\cdot}$	61.5	3.938	0.45	0.55	120.5
$\text{RO}_2^{\cdot} + \text{CH}_2=\text{CHX} \longrightarrow \text{RO}_2\text{CH}_2\text{C}^{\cdot}\text{HX}$	90.5	5.034	0.63	0.36	150.4
$\text{R}^{\cdot} + \text{HOR}^1 \longrightarrow \text{RH} + \text{R}^1\text{O}^{\cdot}$	55.4	3.572	0.56	0.44	99.7
$\text{R}^{\cdot} + \text{O}=\text{CR}^1\text{R}^2 \longrightarrow \text{ROC}^{\cdot}\text{R}^1\text{R}^2$	68.1	3.540	0.61	0.39	112.2
$\text{H}^{\cdot} + \text{HOR} \longrightarrow \text{H}_2 + \text{RO}^{\cdot}$	38.3	2.812	0.53	0.47	33.5
$\text{H}^{\cdot} + \text{O}=\text{CR}^1\text{R}^2 \longrightarrow \text{HOC}^{\cdot}\text{R}^1\text{R}^2$	102.9	4.401	0.61	0.38	149.7

force constant of the bond being attacked (the force constant of a multiple bond is always greater than that of a single bond).

It is expedient to describe the variation of the activation energy of a radical reaction as a function of the reaction enthalpy by the derivative dE/dH at $\Delta H_e = 0$. This value is determined by the parameter α : $(dE/dH) = \alpha(1 + \alpha)^{-1}$. For abstraction reactions, it can be greater than, smaller than, or equal to 0.5. For addition reactions, this ratio is always greater than 0.5 because the force constant of a multiple bond is always greater than that for a single bond. Thus, the activation energy of addition depends on ΔH to a greater extent than the activation energy of abstraction.

The ratio $(r^\ddagger/r_e)_0 = (1 + \alpha)^{-1}$ characterises the position of the transition state on the segment r_e for $\Delta H_e = 0$. Any of the possible cases can be found among abstraction reactions — the $(r^\ddagger/r_e)_0$ ratio can be equal to, greater than, or smaller than 0.5. In the case of addition, $(r^\ddagger/r_e)_0 < 0.5$, i.e., an early transition state is always formed. As in the previous case, this is due to the fact that the force constant of a multiple bond is always higher than that of the σ bond arising and α is always > 1 .

XVI. Conclusion

The use of the parabolic model as a tool for the analysis of addition reactions proved to be exceptionally fruitful. This method provides the possibility of elucidating a number of characteristics and factors influencing the activation energy of addition, based on experimental data. The following factors were found to be the most important.

1. Reaction enthalpy ΔH_e . The dependence of the activation energy E_e on ΔH_e obeys a parabolic law, $\Delta E_e^{1/2} \sim \Delta H_e$. When the ΔH_e value is rather low ($\Delta H_e \leq \Delta H_{e\min}$), the activation energy does not depend on ΔH_e and is close to zero ($E = 0.5 RT$). The parameters b_r calculated from experimental data make it possible to determine E_e for any reaction of the given subclass.

2. Force constants of the reacting bonds (the b_i and b_r coefficients). The activation energy of a thermally neutral reaction E_{e0} is proportional to $[b_i b_r (b_i + b_r)^{-1}]^2$. Depending on which bonds are reorganised during the reaction, the activation energy can change by a factor of 2 due to the difference in the force constants of the reacting bonds alone (the b_i and b_r coefficients).

3. A significant role is played by the arrangement of atoms of the reaction centre. In the case of addition, it is non-linear (triangular); naturally, this affects the activation energy.

4. A substantial contribution to the activation energy is made by the energy of the non-bonding orbital of the resulting bond due to the triplet repulsion in the transition state. The stronger the bond being formed (D_e), the higher the activation energy E_{e0} . For reactions of the same class ($b = \text{const}$ and $\alpha = \text{const}$), $E_{e0} \sim D_e^2$; for reactions of different classes, the empirical dependence (17) holds.

5. Yet another factor is also related to the triplet repulsion, namely, the dependence of E_{e0} on the π bonds present in the vicinity of the reaction centre. This proximity increases the activation energy by 6–15 kJ mol⁻¹. A π bond near the reaction centre increases the electron density on the reaction centre, which increases the energy of the non-bonding orbital and, correspondingly, its contribution to the formation of the activation barrier.

6. The radius of the atom carrying the free valence and attacking the double bond is also significant and influences the activation barrier. The dependence of E_{e0} on the length of the bond being formed $r(C-X)$ is also non-linear [see Eqn (20)].

The activation energies of some subclasses of addition reactions also depend on several other factors, namely, the interaction of polar groups of two polar reactants (among the reactions studied, the contribution of the interaction of polar groups contained in the radical and in the molecule to the activation energy ranges from -25 to +15 kJ mol⁻¹); the multidipole interaction of several polar groups, and the steric factor.

Thus, in the case of both radical abstraction and radical addition, we come across a large variety of factors that influence

the reactivity of the reactants. The parabolic model makes it possible to identify these factors and to characterise the contribution of each of them to the activation energy in terms of an appropriate increment.

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Effects of ultrasound on catalytic processes

M G Sulman

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Abstract. The results of studies on sonochemical catalytic reactions are generalised. The effects of ultrasound on processes of preparation, activation and regeneration of catalysts as well as its influence on the course of catalytic reactions are considered. The advisability of ultrasonic treatment in different stages of catalytic processes is discussed. The bibliography includes 143 references.

I. Introduction

The effect of ultrasonic waves on chemical reactions was first revealed in 1927.¹ The number of publications devoted to studies of reactions which change considerably their rates or direction in an ultrasonic field is increased every year. As regards their sensitivity to acoustic vibrations, all sonochemical reactions may be divided into two groups: some reactions are accelerated in an ultrasonic field and can also occur in its absence, though at a lower rate, whereas others cannot occur at all without the action of ultrasound vibrations. For both groups of reactions, high-frequency (2–10 MHz), medium-frequency (20–100 kHz) and low-frequency (from 10 Hz) vibrations are applied.^{1–7} The classification of sonochemical reactions proposed by Margulis² envisages their following division:

- redox reactions in aqueous solutions between solutes and the products resulting from ultrasonic degradation of water (H, OH, H₂, H₂O₂);
- reactions between dissolved gases and substances in the vapour state under high pressure inside cavitation bubbles;
- chain reactions induced not by radical products obtained upon ultrasonication of water, but rather by another compound present in the system which is split upon cavitation;
- reactions involving macromolecules, including oscillatory reactions which acquired wide popularity in recent years;^{1,8}
- sonochemical reactions in non-aqueous systems;
- initiation of explosion in liquid and solid explosives.

According to this classification, nearly all the catalytic processes can be referred to the reactions in non-aqueous systems, because the main solvent or reagent in them is an organic substance, although water can also participate. For this reason, it seems more appropriate to divide catalytic processes with regard

to the type of catalysis (*e.g.*, homogeneous, heterogeneous) and also to classify them by the type of catalyst and the kind of reaction (hydrogenation, oxidation, *etc.*). This approach has been used in fundamental studies on sonochemistry^{1–5,9} and has become classical in the theory of catalysis.^{10,11} It was proposed to divide the results of the impact of acoustic vibrations on chemical processes into the so-called effects of the first and the second order.^{12–14} These are non-linear effects developing in a liquid upon propagation of high-intensity acoustic waves. However, this approach does not allow estimation of the extent of the influence of individual parameters of ultrasound on chemical reactions. Nonetheless, the equations describing each of these parameters and effects can be used for formalising the problems of mathematical simulation of the corresponding chemical processes.^{9,15}

The action of acoustic vibrations is highly diverse.¹⁶ Ultrasonic waves can accelerate chemical reactions owing to emulsification of liquid components,¹⁷ dispersion of solid components and catalysts, erosion of their surfaces, degassing, prevention of sedimentation or coagulation of the products, intense mixing, *etc.*^{18–20} The action of ultrasound on solid catalysts is far from being always reduced solely to dispersion, since under definite conditions their activities are much higher than those which could be expected after mere grinding of particles.^{1–3} Dispersion results in the increased interface area of reactants and occurs due to both the fragmentation of solid phase particles and the surface friction between the solid and liquid phases.^{21,22} As the thickness of the diffusion boundary layer is decreased, the number of effective collisions between the molecules of reactants is increased.²³ Erosion of solids under the action of low acoustic frequencies has the following feature: the use of medium- and high-frequency acoustic fields crumbles out rather large particles from the surface and it becomes rough, whereas low frequencies cause smoothing and ‘polishing’ of the surface, apparently owing to the crumbling out of microscopic particles.^{2,24,25}

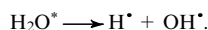
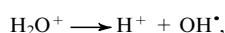
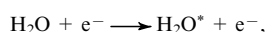
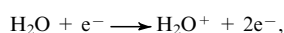
The increase in the rates and selectivities of most chemical reactions in ultrasonic fields appears to be due to the occurrence of cavitation:^{26–29} acoustic waves induce the formation and growth of vapour/gas bubbles in a liquid, which oscillate, pulsate and coalesce. There are two basic approaches to the explanation of high-energy effects caused by cavitation, *viz.*, the thermal and electrical ones. In the thermal approach, these effects are associated with high temperature inside a cavitation bubble upon its adiabatic compression at a continuously increasing rate, whereas in the electrical approach these are related to a discharge inside the bubble resulting from the accumulation of electric charges on its walls.^{1,2,6,12} The electrical action of ultrasound can be exempli-

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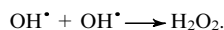
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fied in the formation of hydrogen peroxide.¹ H₂O₂ is generated in microbubbles upon electric discharge in water vapour. First, the elementary processes of ionisation and excitation take place:



Hydrogen peroxide is formed upon recombination:



Hydrogen peroxide cannot be obtained by adiabatic compression of water vapour and a noble gas since this process occurs at high temperature. Hydrogen peroxide decomposes at a lower temperature than does water and therefore is not accumulated to an appreciable extent if only the thermal factors are involved in the adiabatic compression of a cavitation bubble under the action of ultrasound.

The effects of ultrasonic action are the reason for the ever-increasing interest in the use of sonochemical methods in organic synthesis and catalysis.^{30–37} Clearly, the necessity of joint investigation of such complex phenomena as catalysis and sonochemical effects does not promise rapid advances in the elucidation of the mechanism of catalysis in an ultrasonic field. Nonetheless, in some instances the action of ultrasound on catalytic processes has been studied in sufficient detail and the number of publications devoted to catalytic reactions in ultrasonic fields is rather large.^{38–46} Most experimental studies merely state the facts of intensification of processes, increased yields of products and higher catalytic activity without considering the mechanisms underlying the ultrasonic impacts leading to the above-mentioned effects.

As organic liquids are widely used as solvents or reagents, studies of sonochemical reactions in non-aqueous systems are of special significance. In most cases, the use of acoustic vibrations intensifies drastically chemical reactions in such systems.^{9, 21, 22, 47–49} Investigations into the mechanisms of sonochemical reactions in non-aqueous systems are complicated for the following three reasons: the results of these reactions are simultaneously affected by usual thermal and sonochemical effects; such processes occur in rather diverse systems; the action of ultrasound also leads to other concomitant physicochemical and colloidal-chemical effects, *e.g.*, emulsification, dispersion of solids, formation of microscopic bubbles, *etc.*

The present review is devoted to the consideration of the effects of ultrasonic vibrations on catalytic systems and catalysts in different stages of preparation for, and implementation of, chemical reactions.

II. Pre-reaction conditioning of catalysts

1. Ultrasonic treatment in the process of catalyst preparation

Acoustic vibrations are applied to the process of catalyst preparation in order to enhance its activity.⁵⁰

Ultrasound influences substantially the properties of platinum and palladium blacks.^{51–53} The blacks prepared by the reduction of H₂PtCl₆ or PdCl₂ with 40% formaldehyde under the action of ultrasonic waves (USW) of different frequencies in the presence of various gases increased their activities 1.5–2-fold compared to that of USW-nontreated blacks. The surface areas of platinum catalysts increased on the average from 15 to 18 m² g^{−1}. The basic characteristics of Pt and Pd blacks are listed in Table 1.

Magnetic susceptibility of catalysts is enhanced under the action of ultrasound. Paramagnetism of 'ultrasonic' blacks obtained under nitrogen is increased appreciably (about twofold), and it is almost not changed in the course of further training of these catalysts in vacuum. X-ray patterns of 'ultrasonic' blacks exhibit noticeable enhancement of the background, which points to the presence of a substantial amount of the atomic metal phase.

Table 1. Relative activity of platinum and palladium blacks prepared by ultrasonication in an atmosphere of different gases.

Preparation conditions		Activity in reactions ^a (%)		
gas medium	frequency /kHz	of H ₂ O ₂ decomposition	of hex-1-ene hydrogenation	of EtOH oxidation
Pt black				
H ₂	3000	195	119	69
N ₂	20	135	113	74
	548	175	104	84
	3000	260	138	140
Air	20	226	90	118
	548	226	87	110
	3000	116	79	125
Pd black				
H ₂	3000	150	150	82
N ₂	20	320	130	240
	548	200	140	135
	3000	100	175	79
Air	20	—	84	—
	548	158	79	173
	3000	58	70	30

^a The activity of USW-nontreated black in the corresponding reaction is taken as 100%.

The increase in the activity of Pt black in hydrogenation of hex-1-ene and oxidation of ethanol may be explained by the catalyst's increased surface. It is noteworthy that in the process of decomposition of H₂O₂ the effect due to USW is ~2.5 times stronger than that related to the increased surface. Consequently, ultrasound has a specific effect on the active centres of the catalyst. In the oxidation of ethanol, the Pt and Pd blacks prepared under definite conditions in an ultrasonic field proved to be less active than the control catalysts.

Probably, the application of an ultrasonic field induces the formation, on the surface of crystals, of the most disordered amorphous phase which contains active centres for decomposition of H₂O₂, whereas in the reactions of hydrogenation of hex-1-ene and oxidation of ethanol the amorphous phase possesses a decreased catalytic activity.⁵¹ The reason for enhanced activities of the ultrasonicated Pt blacks in the catalytic decomposition of hydrogen peroxide and their relatively low activities in the reactions of hydrogenation and oxidation consists in virtually all the amorphous phase being active in the reaction of decomposition of H₂O₂ since this simplest reaction can occur on active centres of any type. On the contrary, hydrogenation or oxidation require active centres with a more ordered structure which are not formed abundantly under the action of ultrasound. The increase of the reaction order¹ of hydrogenation of hex-1-ene on the ultrasonicated Pt black from zero to first order points to changes in the reaction mechanism. Thus, when discussing an increase or a decrease in the activity of a heterogeneous metal catalyst under the action of ultrasound, it should be indicated to what kind of reaction these changes are referred. This circumstance first established by Kobozev *et al.*⁵¹ should be taken into account in studies of heterogeneous catalytic systems.

As can be seen from Table 1, the nature of gases used in the preparation of blacks has a similar influence on different catalysts. Thus in the decomposition of H₂O₂, the blacks obtained under nitrogen are the most active. The blacks prepared in an ultrasonic field in air are noticeably deactivated possibly due to the adsorption on their surface of nitrogen oxides formed with the participation of the water sonolysis products.⁵³ Deactivation of 'ultrasonic' catalysts prepared in air is most strongly manifested in the hydrogenation reactions. Apparently, the enhanced chemisorption of nitrogen oxides and oxygen in an ultrasonic field

Table 2. Activity of platinum blacks ($\text{mmol s}^{-1} \text{g}^{-1}$) prepared by the reduction of H_2PtCl_6 solutions of different concentrations with hydrogen using ultrasonic fields and mechanical stirring.

Concentration of H_2PtCl_6 (mass %)	Decomposition of H_2O_2		Hydrogenation of hex-1-ene	
	I	II	I	II
0.05	0.37	0.72	—	—
0.10	0.28	0.14	0.19	0.25
0.25	0.21	0.065	0.17	0.071
0.50	0.27	0.062	0.068	0.049

Note. I, mechanical stirring; II, ultrasonication.

prevents the hydrogen uptake by the catalyst and reduces its hydrogenation activity.

It is noteworthy that the catalysts obtained from dilute solutions in an ultrasonic field are more active in the reactions of decomposition of H_2O_2 and hydrogenation of hex-1-ene (Table 2) than those prepared in the absence of USW. It appears that upon reduction of dilute solutions of H_2PtCl_6 in an ultrasonic field the dispersive action of ultrasound is better manifested, whereas upon reduction of concentrated solutions the effects of acceleration of crystallisation and coagulation under the action of ultrasound are predominant.⁵¹ One should, however, bear in mind that the results of studies^{51–53} were interpreted in terms of N I Kobozev's theory of active ensembles, which was not fully confirmed subsequently in the theory and practice of catalysis.

Some specific effects appear under the action of ultrasound in the process of preparation of adsorption catalysts.^{52,53} For example, ultrasonication (frequency 550 kHz, flux density 5.4 W cm^{-2}) of a system H_2PtCl_6 –silica gel, in which the support does not virtually adsorb H_2PtCl_6 , in a hydrogen atmosphere leads to the formation of a mechanical mixture of platinum black and silica gel, whereas in a system H_2PtCl_6 –alumogel, in which the support adsorbs H_2PtCl_6 well, the latter is reduced directly on alumogel under the action of ultrasound. The catalyst thus obtained is active in the hydrogenation of hex-1-ene, whereas the alumogel adsorption catalyst prepared without ultrasonication is inactive.

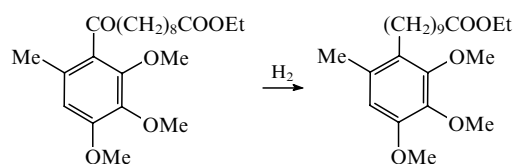
Ultrasound is successfully used for the preparation of catalysts supported on silica gel, alumina or lamellar inorganic materials. Thus the reduction of ammonium hexachloroplatinate in an acoustic field (frequency 440 kHz, intensity 5 W cm^{-2}) in the presence of suspended silica gel leads to an 80% increase in the surface of the metal compared to that of a sample obtained by mechanical stirring. This may rationalise the increase in the activity of highly dispersed catalysts $\text{Pd}/\text{Al}_2\text{O}_3$ or Pd/C in the reaction of reduction of acetophenone by hydrogen.⁵⁴

One of the stages in the proposed mechanism of catalytic hydrogenation is migration (spillover) of hydrogen to the adsorbed substrate molecules.⁵⁵ This explains the enhancement of the activity of a Pd/C catalyst obtained by the reduction of a palladium salt with formaldehyde under the action of ultrasound in the reaction of hydrogenation of nitrobenzene at 303 K.⁵⁶ In the case of ultrasonic treatment, the amount of hydrogen capable of participating in the spillover increases appreciably: after ultrasonication of the Pd/C catalyst (0.8 mass % Pd) the H : Pd ratio may reach 6.8.

Preliminary ultrasonic treatment of a Pt/SiO_2 catalyst intended for the hydrogenation of cinnamaldehyde resulted in a considerable increase in the selectivity of formation of cinnamic alcohol (up to 80%) and a twofold increase in the reaction rate. This effect is explained⁵⁷ by the formation on the support of effective metal centres providing for stronger substrate adsorption involving the $\text{C}=\text{O}$ bond.

Comparative studies of the profound reduction of the $\text{C}=\text{O}$ groups on H_2SO_4 -unmodified and -modified Pt catalysts with and without ultrasonic treatment also confirmed the activating action

of USW.^{58,59} This conclusion was drawn from the results of hydrogenation of the carbonyl group of ethyl 9-(2,3,4-trimethoxy-6-methylbenzoyl)nonanoate on a Pt/sibunit catalyst.



In the course of the experiment, the extent of the catalyst dispersion was monitored by a conductometric method. Analysis of the results obtained allowed one to conclude that the granulometric composition of the catalyst remained invariant under the action of USW with the intensity of up to 1 W cm^{-2} , while the reaction rate increased as the duration of ultrasonic pretreatment was prolonged from 15 to 30 s. The catalyst subjected to the USW action for 60 and 120 s exhibited lower activity. The increase in the ultrasonic flux density from 0.1 to 1 W cm^{-2} favoured the catalyst's activity, while its further increase to 3 W cm^{-2} resulted in the decrease in activity (Fig. 1). Deactivation of the catalyst upon increase in the duration and intensity of sonication may be explained by the restructuring of active centres associated with an appreciable modification of the morphology of the catalyst's surface. Examination of the catalyst's samples before and after sonication by electron microscopy confirmed this conclusion, which is in full agreement with the data reported by Garibyan *et al.*²⁵ X-Ray photoelectron spectroscopic data showed that the $\text{Pd(II)} : \text{Pd(0)}$ ratio increased after ultrasonic treatment. Assuming that the hydrogenation of the $\text{C}=\text{O}$ group proceeds on a bifunctional active centre $\text{Pd(0)}-\text{Pd}^{\delta+}$, the higher catalyst activity may be explained by the increased proportion of Pd(II) under the action of USW.^{31,32}

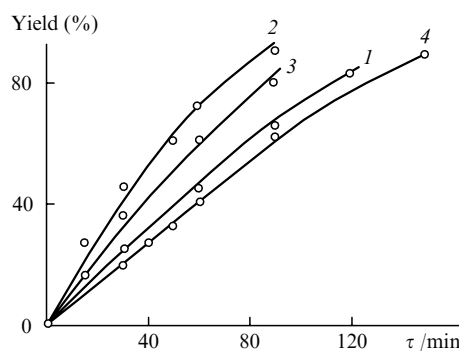


Figure 1. Dependence of the yield of the hydrogenation product of ethyl 9-(2,3,4-trimethoxy-6-methylbenzoyl)nonanoate on a Pt/sibunit catalyst on the reaction time (τ) and the USW intensity (W cm^{-2}): (1) 0.1; (2) 1; (3) 3; (4) without USW. The duration of ultrasonication was 30 s.

Systematic investigations of the impact of ultrasound on novel polymeric palladium catalytic systems containing metal colloids have led to a conclusion about an appreciable effect of acoustic vibrations on the activity of these catalysts in the selective hydrogenation of the triple bond of acetylenic alcohols to the double bond.^{60,61} High dispersion of the catalyst's active phase was attained also by ultrasonication in the stage of preparation of supported ruthenium catalysts.⁶² Ultrasound has a strong effect on the genesis and properties of alumogel,⁶³ which is widely used as the support for hydrogenation and dehydration catalysts and also as the support for the active phases of adsorption catalysts. The application of an ultrasonic field accelerates crystallisation of alumogel and its surface is increased by 40% compared to that of ultrasound-nontreated samples. This results in the formation of a secondary structure consisting of smaller aggregates with a

strongly developed surface and in higher hydrophilicity of particles, which prevents their aggregation.

The relevant literature carries a suggestion that cleavage of the carbon–carbon bonds occurs after their activation on ‘metal’ active centres.⁵⁵ The number of such centres appears to increase as a result of changes in the dispersion under the action of ultrasound leading to the acceleration of hydrogenolysis. Supported palladium and rhodium catalysts prepared on the base of TiO₂–SiO₂ gels under ultrasonic treatment possess higher activity than analogous systems non-treated with ultrasound and ensure the required selectivity in the hydrogenolysis of n-butane.⁶⁴

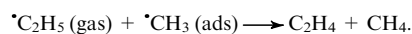
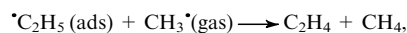
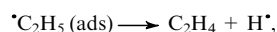
The catalytic activity of nickel obtained by the reduction of nickel oxalate at 583 K under the action of acoustic vibrations with a frequency of 25 kHz and an intensity of 3000 W cm^{–2} is increased by 87% in the reaction of hydrogenation of benzene (see Ref. 9). Probably, as in the case of Pt and Pd,^{5,59} this is related to the modification of the structure of the catalyst’s surface under the action of ultrasound. Similar effects were also observed when other nickel catalysts were used. Sonication in the course of reduction of nickel iodide with lithium has led to activated nickel which catalysed 1,4-addition of phenylsilane to α,β -unsaturated ketones and nitriles providing high yields (after hydrolysis) of hydrogenation products.⁶⁵ Activated nickel powder is also used in the synthesis of aminoarenes by reduction of nitroarenes. This catalyst is prepared by the reduction of anhydrous nickel chloride with potassium subjected to dispersion by ultrasound.⁶⁶

Ultrasonication gives a positive effect in the preparation of promoted and supported oxide catalysts which are used in the oxidative addition of methane (Na₂O–ZnO, Li₂O–MgO, La₂O₃–MgO, Sm₂O₃–MgO), oxidation of propylene (Na₂O–ZnO) and total oxidation of methanol to CO₂ (CuO–SiO₂).⁶⁷ Application of USW in the stage of impregnation increases the catalytic activity of oxides in oxidative processes. The use of the 10% Na₂O–ZnO catalyst thus obtained increases the methane conversion from 14% to 18% and raises the selectivity from 40% to 54%. On the activated 1% La₂O₃–MgO catalyst, the degree of conversion is increased insignificantly, whereas the selectivity is increased from 54% to 60%. The C₂H₄:C₂H₆ ratio is changed in favour of ethylene. A similar effect of an increase in the catalytic activity of manganese and chromium oxides was also observed in the heterogeneous oxidation of 1-hydroxyphosphonates.⁶⁸

According to Garibyan *et al.*,⁶⁷ the improvement of catalytic properties of oxides upon sonication may be due to changes in the number and structure (composition) of active centres, which is in agreement with the conclusions⁵² drawn from the study of oxidation of ethanol on platinum and palladium. The electron microscopy analysis of samples prepared with and without application of USW has shown that the application of ultrasound provided a more uniform distribution of components. This inference is consistent with the results of analysis of palladium catalysts.^{24,25} Promoter oxides present on ZnO or MgO in the form of agglomerates are dispersed on the support surface. The promoter increases the efflux of $\cdot\text{CH}_3$ and $\cdot\text{C}_2\text{H}_5$ radicals to the gas phase;⁶⁹ consequently, a uniform distribution of sodium and lanthanum ions reached under the action of USW favours the formation of radicals and prevents their capture by the surface. This results in an increased yield of C₂ hydrocarbons.

The use of the EPR method has shown that the activation of methane and ethane on ultrasound-treated catalysts provides higher concentrations of free radicals in the gas phase. On the USW-nontreated Sm₂O₃–MgO catalyst, the ratio of desorbed radicals [$\cdot\text{CH}_3$]:[$\cdot\text{C}_2\text{H}_5$] is equal to 0.9, whereas upon ultrasonication it increases to 1.75. This implies that in the latter case additional disintegration processes with the release of C₂H₄ take place in the course of formation of $\cdot\text{C}_2\text{H}_5$ radicals. Experiments on CH₄ conversion under atmospheric pressure showed that under the action of USW the [C₂H₆]:[C₂H₄] ratio is shifted in favour of ethylene. The ethyl radicals are decomposed either on the surface

or in the gas phase, *i.e.*, a radical mechanism without participation of a solvent is realised:



Incorporation of ions of a different valence (M⁺) into the lattice of alkaline-earth metal oxides leads to changes in the defect structure of the catalyst and its higher activity in the process under study. Ultrasonication results in the enhancement of this effect.

The extent of oxidation of propylene on the Na₂O–ZnO catalyst activated by 60-min ultrasonication increased by 4% compared to that on the USW-nontreated catalyst; the composition of products also changed.⁶⁷ the yield of hexadiene increased, while the amount of hydrogen and benzene decreased (Table 3). The Na₂O–ZnO system contains numerous unprotected ZnO centres on which oxidation does take place. Considerable content of hydrogen in the products is related to the possible dehydroaromatization of hexadiene on zinc oxide. In the catalyst subjected to the action of USW, sodium oxide covers the surface of zinc oxide uniformly and suppresses this process thus increasing the yield of hexadiene.

Table 3. Composition of the propylene oxidation products on a 10% Na₂O–ZnO catalyst. Reaction conditions: temperature, 843 K; contact time, 5.5 s; pressure, 1 atm.

[C ₃ H ₆] (vol.%)	Con- version (%)	Conditions of catalyst treatment	Composition of products (vol.%)				
			CO + CO ₂	H ₂	C ₂ H ₆	(C ₃ H ₅) ₂	MeOH
3.5	30	mechanical stirring	8.32	2.7	0.112	0.01	0.081
3.9	33.9	ultra- sonication	9.00	0.5	0.082	0.08	0.103

The same approaches were used in studies of the total oxidation of methanol on the 5% CuO–SiO₂ catalyst. The data on the temperature dependence of conversion of methanol in this system are listed in Table 4. The selectivity of CO₂ formation was found to be equal to 100% at all the temperatures studied. As can be seen from Table 4, irrespective of the SiO₂ porosity (catalysts 1 and 2 have the pore size 10²–10⁵ and 10–100 Å, respectively), the ultrasonic treatment in the stage of catalyst preparation increased the degree of conversion, which reached 86% at 668 K. The ultrasound-treated catalysts preserve their activities for a prolonged time. The phase composition of catalysts prepared by the method of thermal treatment at 623 K with and without sonication was also studied. The diffractograms of the catalysts of oxidation of methanol that have operated for the same time period point in both cases to the presence of only CuO phase,

Table 4. The temperature dependence of the methanol conversion into CO₂ on the 5% CuO–SiO₂ catalyst (1.5 vol.% MeOH in air).

Conditions of treatment	Conversion (%) at the temperature/K				
	573	598	623	648	668
Sample No. 1					
Mechanical stirring	20	43	56	66	75
Ultrasonication	43	60	65	77	86
Sample No. 2					
Mechanical stirring	33	43	48	67	73
Ultrasonication	40	50	66	70	86

although the activity of the ultrasound-treated catalyst remains at a high level. The sonication favours uniform distribution of the CuO phase over the SiO₂ surface. The CuO–SiO₂ samples prepared at 623 K with and without ultrasonication were studied before and after the reaction by the EPR method. The concentration of paramagnetic Cu²⁺ ions in the catalyst ultrasonicated before the reaction was one order of magnitude higher than that in the catalyst prepared in the usual manner. After the reaction, nearly equal low concentrations of copper ions were found on both catalysts. This may be explained by the degradation of the intermediate Cu₂(OH)₃NO₃ phase into CuO during the reaction.

Thus, the application of ultrasound for the preparation of promoted and supported catalysts enhances appreciably the efficiency of catalytic systems.

Ultrasonication of a suspension in the co-precipitation and ageing of copper, zinc and aluminium oxides enhanced noticeably the activity of the catalyst of methanol synthesis.⁷⁰ It was suggested that under the action of ultrasound the Cu:Zn:Al ratio in the catalyst precursor becomes the same as in the compound Cu₃Zn₃Al₂(OH)₁₆CO₃·4H₂O, *i.e.*, 3:3:2. The specific surface of the thus obtained highly dispersed Cu(Cu⁺), ZnO and Al₂O₃ particles as well as the yield of methanol depend linearly on the content of this hydrate-like phase.

Ultrasound is also used in the stage of precipitation in the preparation of catalysts and their precursors.⁷¹ Formation of agglomerates in mixed half-precipitated suspensions of (Cu/Zn)₂(OH)₂CO₃ under the action of acoustic waves of different intensity was studied. The application of ultrasound influences substantially the size of particles and the surface of agglomerates. The precursors precipitated by the low-intensity ultrasonication have basically small specific surface and are composed of small agglomerates. The precursors prepared using high-intensity USW are characterised by a more developed surface and formation of larger agglomerates. The MnO₂ catalyst prepared under the conditions of high-intensity ultrasonic treatment possesses higher activity as regards evolution of oxygen from H₂O₂ than that of an analogous but USW-nontreated catalyst.

The ultrasound treatment is also used for the preparation of electrode catalysts of the solid-oxide fuel cell.⁷² For example, the anode catalyst La_{1.8}Al_{0.2}O₃ is prepared by pyrolysis of an aqueous mixture of lanthanum and aluminium nitrates. This technique provides higher activity of the anode catalyst than that attained using other methods. The optimum conditions for the ultrasonic treatment are determined experimentally by monitoring the particle size and from the dependence of the quantity of deposited particles and their size on the concentration of an aqueous solution and temperature.

There is a possibility of sonochemical synthesis of various nanostructured materials using high-intensity ultrasound.⁷³ In the decomposition of organometallic compounds under the action of ultrasound, the specific surface of the solid phase composed of agglomerates and nanoclusters is increased. This technique was used to synthesise nanostructured metals and alloys from iron pentacarbonyl and cobalt tricarbonylnitrosyl; molybdenum carbide was prepared in this way from molybdenum hexacarbonyl. These materials represent active heterogeneous catalysts for reforming of hydrocarbons and hydrogenation of CO.

The use of surface acoustic waves and resonance vibrations makes it possible to prepare heterogeneous catalysts with artificially controllable functions.⁷⁴ For instance, thin films of catalysts were precipitated using horizontal surface-active waves generated on ferroelectric single crystals of LiNbO₃ and LiTaO₃. This resulted in an appreciable increase in the activities of Ag, Pd and Ni catalysts in the oxidation of ethanol and of Pd catalyst in the oxidation of CO. The enhancement of catalytic activity is related to the modification of the coefficients of electromechanical adhesion of ferroelectrics and to the state of the catalyst surface.

It should be noted that ultrasound not only influences the process of catalyst preparation but also enhances the activities of ready-to-use catalysts in various reactions.⁵⁹

2. The action of ultrasound on ready-to-use catalysts

Ultrasonication influences the genesis of crystalline catalysts, their properties and catalytic activities in various reactions and favours the increase in the size of solid particles irrespective of the nature of the material used.⁷⁵ An appreciable decrease in the particle size is particularly noticeable at a low metal content.⁷⁶ The removal of impurities from the metal surface makes an additional contribution to the enhancement of the catalyst's activity.⁵⁹

Asymmetric catalysis on metals implies the interaction of a substrate with an active centre formed as a result of coordination of a chiral modifier with the metal component of the catalyst.⁷⁷ Ultrasonic treatment of catalysts leads to an increased enantioselectivity of many processes, *e.g.*, hydrogenation of ethyl pyruvate to ethyl lactate on various platinum catalysts (Pt/C, Pt/Al₂O₃, Pt/SiO₂ and Pt/montmorillonite).⁷⁸ After the action of USW on the Pt/SiO₂ and Pt/montmorillonite catalysts, the enantioselectivity is enhanced substantially, the hydrogenation rate is increased by an order of magnitude compared to that on the untreated catalyst, while the yield of the target product reaches 100%. The enhanced activity can be due to the decreased size of the catalyst's particles (Table 5) and changes in their morphology. Initially, the size of platinum crystals ranges from 5 to 60 nm. After ultrasonication, small particles (3–5 nm) become predominant and their distribution is almost uniform. Apparently, this favours the formation of a large number of reactive different-ligand complexes and, consequently, enhances the catalyst's activity. Analogous results were obtained in the sonochemical treatment of a catalytic system Pt/Al₂O₃–quinidine in acetic acid.⁷⁹ In addition, sonication made possible the repeated use of the catalyst without its regeneration, *i.e.*, made the catalyst more stable.

Table 5. Mean diameter of metal particles in supported platinum catalysts before and after 30-min ultrasonication.⁷⁸

Catalyst	Diameter of particles /nm	
	before treatment	after treatment
5% Pt/C	3.0	2.5
3% Pt/SiO ₂	6.7	4.2
5% Pt/montmorillonite	3.7	3.8
5% Pt/Al ₂ O ₃	23.1	12.6

A number of studies were devoted to the investigation of the ultrasonic treatment of Raney nickel.^{22, 80–87} Sonication in water⁸⁰ with subsequent asymmetric modification yielded a highly efficient catalyst of enantioselective hydrogenation. The complex tartaric acid–NaBr–modified Raney nickel exhibits high enantioselectivity and catalytic activity in the hydrogenation of β-diketones and β-keto esters.^{81, 82}

According to Suslick and Casadonte,²² ultrasonic treatment (20 kHz, 50 W cm^{–2}) of a nickel powder (particle size 5 μm) in octane increased 10⁵ times its ability to catalyse hydrogenation of alkenes. Though, such a strong effect is in part due to the fact that the results were compared with an inactive form of nickel. The application of an acoustic field simplifies considerably the preparation of the catalyst. The initial hydrogenation rate reaches its maximum after preliminary 60-min ultrasonication of a sample, whereas further action of ultrasound decreases its catalytic activity (Fig. 2). The use of scanning electron microscopy showed that the acoustic field does not modify the particle size but influences noticeably the surface morphology. Sonolysis allows preparation of nickel with a specific surface close to that of Raney nickel. Initially, the surface of the crystalline structure is smoothed under the action of ultrasound and then the particles 'stick' to each other,^{22, 86} which is presumed to be the main reason for the decrease in the hydrogenation rate upon prolonged action of ultrasound. However, the effect of particle sticking is difficult to explain from the physical viewpoint, since for this process to occur, the particles should be heated to their melting temperature,

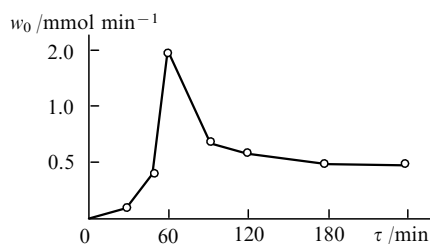


Figure 2. Dependence of the initial rate of hydrogenation of non-1-ene (w_0) on the duration of ultrasonic activation (τ) of nickel powder; temperature 273 K, pressure 1 atm.

which is possible if their minimal relative speed at the moment of collision¹ is $15\,000\text{ m s}^{-1}$, which is 30 times as high as the really observed one (500 m s^{-1}) and almost 10 times higher than the velocity of sound propagation in the liquid.

The ultrasound-treated platinum (mainly Pt/C), nickel and palladium catalysts are successfully used in reactions of hydrogenation and hydrosilylation of alkenes.^{83–85}

A catalytic system metal hydride–dialkylzinc activated by ultrasound is effective in the reduction of carbonyl compounds and epoxides (like the ultrasound-nontreated system) and in reactions of partial reduction of carboxylic acids to aldehydes.⁸⁸ This system is highly attractive owing to its accessibility, inexpensiveness and simplicity of handling and, hence, it may be particularly useful for the implementation of large-scale reduction processes.

The possibility of ultrasonic activation of polymerisation, aldol condensation, allylation and oxidation catalysts should also be noted. Ultrasonic treatment (20–500 kHz, 4–20 W cm^{-2}) of octane-suspended titanium trichloride, belonging to the group of the Ziegler–Natta catalysts, led to the decrease in the particle size from 15–40 to 0.1–5 μm . Crystalline polymers formed in the presence of this catalyst are more uniform with regard to their molecular mass than are polymers obtained on the ultrasound-nontreated catalyst. Similar results were also derived using other Ziegler–Natta catalysts.⁵ The application of ultrasound enhances the catalytic activity of the metal iodide-promoted BiCl_3 used as the catalyst of the Mukaiyama and Mukaiyama–Michael reactions.⁸⁹ The ultrasound has an accelerating effect on the systems BiCl_3 –1.5 ZnCl_2 or BiCl_3 –1.5 SnI_2 (5 mol. %), which catalyse the crossover aldolisation of acetophenone and benzaldehyde.

Ultrasound-activated palladium catalyses the heterogeneous allylation of carbonyl compounds with γ -substituted allyl alcohols in the presence of SnCl_2 in non-polar solvents (diethyl ether, diisopropyl ether and toluene).⁹⁰ The reaction proceeds regioselectively with high yields of 1,4-disubstituted but-3-en-1-ols; the regioselectivity (α -selectivity) of the reaction on ultrasound-activated palladium is the opposite of the regioselectivity (γ -selectivity) of the palladium-catalysed homogeneous carbonyl allylation in polar solvents.

Gariyban *et al.*²⁵ studied the effect of ultrasound in the stage of preparation of catalysts on their activities and selectivities in the oxidative condensation of methane, oxidation of propylene on $\text{Na}_2\text{O}/\text{ZnO}$ and profound oxidation of MeOH on CuO/SiO_2 .

It is noteworthy that the most interesting results were obtained when the ultrasound was involved in catalytic processes.

III. Sonochemical catalysis

1. Homogeneous catalysis

The application of ultrasound with the intensity sufficient for inducing cavitation leads to the acceleration of chemical reactions, which appears to be determined by the formation of free radicals.⁹¹

An extensive series of homogenous catalytic processes carried out under sonication have been studied. Thus Müller *et al.*⁹² demonstrated the possibility of the ultrasound-induced highly effective enantioselective chain elongation of labile fluorenylmethoxycarbonyl-protected amino acids by means of Wolf rearrangement of the corresponding α -diazo ketones at room temperature catalysed by silver ions. Donatti and Vollet⁹³ investigated hydrolysis of tetraethoxysilane at 312 K and mixtures of tetramethoxysilane and tetraethoxysilane at 308 K catalysed by hydrochloric or oxalic acid in an ultrasound field. It was shown that Lewis acids or sonication catalyse the condensation of imines with H-phosphonates bound to the Wang resins resulting in high yields of the corresponding α -aminoalkylphosphonates.⁹⁴ A number of diterpenoids were obtained by highly regioselective cycloaddition of styrenes to substituted 1,4-benzoquinones under the action of ultrasound in the presence of Lewis acids as catalysts.⁹⁵ The application of ultrasound increased appreciably the rate of addition of aldehydes to methyl acrylates catalysed by 1,4-diazabicyclooctane.⁹⁶ Ultrasonic waves with an amplitude of 120 μm accelerate decomposition of 2-chlorophenol in the presence of 200 mg litre^{-1} of H_2O_2 .⁹⁷ Under the action of ultrasonic vibrations, the condensation of indene or 2-nitrofluorene catalysed by bis(*p*-methoxyphenyl) telluroxide leads to the corresponding fulvenes in high yields.⁹⁸ Ultrasound is also used in the reactions involving fatty acids.⁹⁹ For example, an isomer of methyl 8-(5-hexyl-4,5-dihydro-3*H*-pyrrol-2-yl)octanoate can be synthesised from methyl ricinoleate in several ways. The highest yield (42%) is achieved and the minimum reaction time is necessary in the case where USW (20 kHz, 53 W cm^{-2}) are applied.

Let us consider in more detail oxidation and isomerisation reactions occurring under the action of USW. The results of studies of the effect of ultrasound on the liquid-phase oxidation of hydrocarbons by the radical-chain mechanism in the presence of 0.3% cobalt stearate are presented in Table 6. It is seen that the accumulation of oxygenated compounds is increased by 15%–30% under the action of USW. As the pressure increases, the oxidation rate also increases. The maximum acceleration of the process is reached at a frequency of $\sim 300\text{ kHz}$. It is of essence that in an ultrasonic field the oxidation rate remains invariant for a long time, whereas without ultrasonic treatment it reaches a maximum and then decreases appreciably. In the process of oxidation, cobalt stearate usually forms a micelle with the hydrocarbon, which is a reason for the decrease in the catalyst's activity. In an ultrasonic field, complexes of this type decompose or are not formed at all, and this prevents shielding of the catalyst by hydrocarbon molecules and enhances their stabilities because of which the reaction rate remains constant.

Table 6. Characteristics of the product of n-tetradecane oxidation at 385 K in the presence of cobalt stearate catalyst.

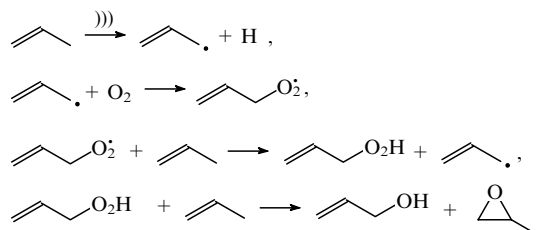
Characteristic	Without ultrasonic treatment	Under the action of ultrasound with a frequency of /kHz		
		300	600	1000
Acid number ^a	21.0	29.2	27.2	25.0
Ester number	10.6	14.9	14.2	13.7
Carbonyl number	22.4	28.1	26.4	27.4
Hydroxyl number	7.2	7.5	6.2	5.5
Sum of oxygenated compounds	61.2	79.1	73.9	71.6

^a In mg KOH per 100 g product.

It is of note that the oxidation rate decreases appreciably at an USW frequency of 16 kHz. This effect may be explained by several reasons: intense degasification of the hydrocarbon at low frequencies and high intensity of irradiation; chemical modification of the

catalyst's molecules; higher decomposition rate of peroxide compounds formed in the oxidation.

Oxidation of alkenes by oxygen in the presence of $\text{Mo}(\text{CO})_6$ with the formation of enols and epoxides was performed under the action of ultrasound.⁵ The primary sonochemical act in this process is presumed to be homolysis of the allylic C–H bond under the action of cavitation.



Under ultrasonic stirring, the homogeneous cationic ferroporphyrins become effective catalysts of cyclohexane oxidation in the presence of MeCN. At a total yield of 93%, the ratio of selectivities of the formation of epoxide, alcohol and ketone is 77 : 12 : 11.¹⁰⁰

Margulis²⁶ investigated the catalytic isomerisation of alk-1-enes into alk-2-enes in an ultrasonic field in the presence of metal carbonyls. In the presence of $\text{Fe}(\text{CO})_5$, isomerisation of pent-1-ene under the USW action (frequency 20 kHz, intensity 100 W cm^{-2}) proceeds at a constant rate for 1 h, then the catalyst's activity drops for a period of several hours due to the formation of dispersed metallic iron and a small amount of $\text{Fe}_3(\text{CO})_{12}$. High initial activity of carbonyl $\text{Fe}_2(\text{CO})_9$ decreases rapidly, since under the conditions of sonolysis it is transformed at a high rate into the complex $\text{Fe}(\text{CO})_5 \cdot \text{Fe}_3(\text{CO})_{12}$; however, even under prolonged exposure to ultrasound the complex does not undergo degradation with the liberation of metallic iron. The initial rate of catalytic isomerisation of pent-1-ene measured 5 min after the beginning of sonication is increased more than 10^6 times compared to the rate in the control experiment (without ultrasound).

It was shown that the efficiency of isomerisation decreases when alk-1-enes have substituents creating steric hindrances (Table 7). Therefore, isomerisation of 2-ethylpent-1-ene and allylbenzene is appreciably slower than that of pent-1-ene. Isomerisation of *cis*-stilbene virtually does not occur because of either the non-terminal position of the double bond or the difficulty of forming an intermediate complex with $\text{Fe}(\text{CO})_5$. According to the data from Table 7, the isomerisation rate of linear alk-1-enes changes in the order: pent-1-ene $\approx$ hex-1-ene $\gg$ oct-1-ene $>$ dec-1-ene.

Isomerisation of alkenes in an ultrasonic field in the presence of other metal carbonyls, not only iron carbonyls, was also studied. It is seen from Table 7 that in the presence of iron carbonyl *trans*- and *cis*-pent-2-enes are formed in the ratio

Table 7. Isomerisation of alk-1-enes in an ultrasonic field in the presence of $\text{Fe}(\text{CO})_5$.

Initial alkene	Products ^a	Relative isomerisation rate
Pent-1-ene	<i>trans</i> -pent-2-ene (77%) <i>cis</i> -pent-2-ene (23%)	1.0
Hex-1-ene	<i>trans</i> -hex-2-ene (74%) <i>cis</i> -hex-2-ene (26%)	1.1
2-Ethylpent-1-ene	2-ethylpent-2-ene	0.31
Oct-1-ene	<i>trans</i> - and <i>cis</i> -oct-2-enes	0.17
Dec-1-ene	<i>trans</i> - and <i>cis</i> -dec-2-enes	0.05
Allylbenzene	β -methylstyrene	0.02
<i>cis</i> -Stilbene	<i>trans</i> -stilbene	0.02

^a Yields are indicated in parentheses.

virtually close to the thermodynamic equilibrium. This ought to be expected, since irrespective of the presence or the absence of the ultrasonic field the same species remain catalytically active. However, in the presence of $\text{Ru}(\text{CO})_5$ and $\text{Ru}_3(\text{CO})_{12}$ other ratios of *cis*- and *trans*-isomers are obtained, which points to a different mechanism of catalytic action of ruthenium carbonyls and to the participation of different intermediates in the reaction. The catalytic activities of carbonyls in the isomerisation reaction under the action of USW decrease in the series: $\text{Ru}_3(\text{CO})_{12} > \text{Fe}(\text{CO})_5 > \text{Mo}(\text{CO})_6 > \text{Fe}_3(\text{CO})_{12} \gg \text{W}(\text{CO})_6 \approx \text{Cr}(\text{CO})_6$. The rates of photocatalytic isomerisation change in a different sequence: $\text{Fe}(\text{CO})_5 > \text{Fe}_3(\text{CO})_{12} > \text{Ru}_3(\text{CO})_{12} > \text{W}(\text{CO})_6 \approx \text{Mo}(\text{CO})_6 \gg \text{Cr}(\text{CO})_6$. In many cases, the ratios of *trans*- and *cis*-isomers in the sonocatalytic and photochemical isomerisations are similar; however, when $\text{Ru}_3(\text{CO})_{12}$ is used, they differ considerably and amount to 2.8 and 6.0, respectively.

These results suggest the existence of substantial differences in the mechanisms of sonochemical and photochemical initiation of the catalytic processes, the catalytic activity being higher in the first case. Experimental data support the suggestion that in both cases the stages in which hydrogen migrates from the β -position of the alkene to form an intermediate hydride, *viz.*, π -allylic complex, are analogous. In accordance with the commonly accepted scheme, sonolysis of $\text{Fe}(\text{CO})_5$ in the presence of an excess of pent-1-ene yields $[\text{Fe}(\text{CO})_4(\text{C}_5\text{H}_{10})]$, which is confirmed by IR spectroscopy.

Exposure to ultrasound not only enhances the rates of homogeneous catalytic reactions, but also increases the number of catalytic cycles. Ultrasound is a factor which influences the catalytic activity of iron(III) *meso*-tetrakis(2,6-dichlorophenyl)porphyrin chloride $[\text{Fe}(\text{TDCPP})\text{Cl}]$ in a homogeneous system¹⁰¹ where cyclohexanol is formed from cyclohexane by a classical mechanism of hydroxylation with the participation of iodosylbenzene: PhIO is reduced to iodobenzene with the oxidation of $[\text{Fe}(\text{TDCPP})\text{Cl}]$ resulting in the formation of catalytically active species of iron(IV)oxoporphyrin radical, which directly hydroxylates cyclohexane. The optimum conditions of this reaction have been established: $[\text{Fe}(\text{TDCPP})\text{Cl}] = 3 \times 10^{-4} \text{ mol litre}^{-1}$ in 1,2-dichloroethane, ultrasonic stirring at 273 K in an excess of PhIO. Ultrasound makes it possible to achieve an unusually high yield of cyclohexane (96%) and to increase more than twofold (from 45 to 96) the number of reaction cycles. The catalyst $[\text{Fe}(\text{TDCPP})\text{Cl}]$ acting in an ultrasonic field may be regarded as a good biomimetic model. This is a stable and selective catalyst allowing the preparation of cyclohexanol as the single product.

Application of an ultrasonic field (35–40 kHz) increases considerably the number of catalytic cycles involving a water-soluble rhodium catalyst for the hydroformylation of alkenes.⁵ The number of such cycles in the preparation of aldehydes under a pressure of 2.5 MPa in an aqueous solution containing a 1 : 1 mixture of carbon monoxide and hydrogen, hex-1-ene and the rhodium complex $\text{HRhCl}(\text{CO})[\text{P}(\text{C}_6\text{H}_4\text{SO}_3\text{H})_3]_3$ under the action of ultrasound is 11.34, whereas with mechanical stirring at a rate of 500 rpm it is 3.24.

Thus, ultrasound accelerates homogeneous catalytic reactions by modifying in some cases their mechanisms and increases the stability of homogeneous catalysts.

2. Heterogeneous catalysis

Acoustic vibrations can exert a dual effect on heterogeneous catalytic reactions. On the one hand, they favour mass transfer and, on the other hand, enhance the activity of catalysts.^{51, 102, 103} The use of ultrasound in heterogeneous reactions opens broad possibilities for the application of physical and chemical factors of acoustic impact. Difficulties of studying such factors are related to the absence of unequivocal and clear-cut concepts of the nature of the ultrasound effect on heterogeneous catalytic processes. At present, several tentative mechanisms of the effects observed may be discussed, but there is no answer so far to the question about which of them is predominant.²⁶

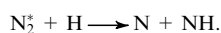
Table 8. Rates of NH_3 formation ($\mu\text{mol litre}^{-1} \text{ min}^{-1}$) in the sonolysis of water saturated with a mixture of N_2 and H_2 in the presence of metal catalysts.⁵¹

Catalyst	Rate of NH_3 formation ^a	Catalyst	Rate of NH_3 formation ^a
Rh (from RhCl_3)	2.5, 3.0	Rh black	1.4, 1.3
Pt (from H_2PtCl_6)	1.6, 2.0	Pt black	1.0, 0.9
Pd (from PdCl_2)	1.3, 1.5	Pd black	0.73, 0.80
Without catalyst	0.4	Rh black (without USW)	0.00

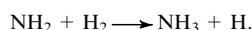
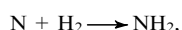
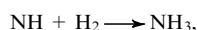
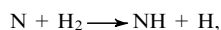
^a In most cases, there are two values derived from parallel experiments.

Let us consider the mechanism[†] of a heterogeneous catalytic reaction in an ultrasonic field exemplified in the synthesis of NH_3 . A remarkable effect has been observed: in water saturated with a mixture of N_2 and H_2 in the stoichiometric proportion, the rate of NH_3 formation under ultrasonic irradiation in the presence of platinum group metals as catalyst is rather high, whereas without ultrasound no reaction occurs whatsoever.⁵¹

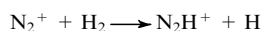
Table 8 lists the rates of the NH_3 formation in the presence of different catalysts in the sonolysis (550 kHz, 4–5 W cm^{-2}) of water saturated with a mixture of N_2 and H_2 . The rate of NH_3 formation in the absence of catalysts is close to the rate of HNO_2 formation in the sonolysis of water in the nitrogen atmosphere (in addition to nitrous acid, H_2O_2 and HNO_3 are also formed as the reaction products).¹⁰⁴ Accordingly, it may be presumed that NH_3 is synthesised in an ultrasonic field non-catalytically in the gas phase with cavitation bubbles involving the excited nitrogen molecules, *e.g.*, the long-living metastable term $\text{N}_2^*(A^3\Sigma_u^+)$



In this case, ammonia is formed according to the following scheme:



It is possible¹⁰⁵ that, as in the case of the reaction in an electric discharge, the primary act in the sonochemical synthesis of NH_3 is the ionisation of nitrogen followed by the stage



and then by the stage which ultimately leads to the formation of ammonia.

Ultrasonic fields accelerate appreciably hydrogenation of unsaturated compounds,⁸¹ *e.g.*, indene, acenaphthylene, non-1-ene, α -methylstyrene and *trans*-benzylideneacetone.

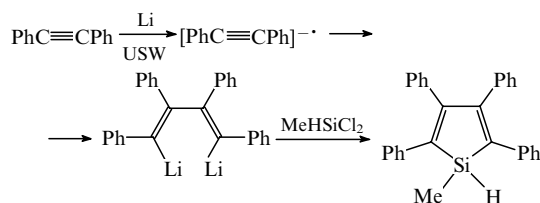
Hydrogenation was carried out on a catalyst obtained by deposition of 10% Pd on activated carbon in the presence of formic acid as the hydrogen carrier. In an ultrasonic field, 100% hydrogenation of the double bonds at 298 K was reached within 1 h, whereas the aromatic rings remained intact. Without ultrasound, the reaction was considerably slower and the yield was 70% after 1 h and 90% after 2 h.

Ultrasonic field increased appreciably the hydrogenation rate of alkenes in anhydrous media in the presence of platinated carbon. It should be noted that the hydrogenation of acyclic

alkenes is accelerated to a greater extent than that of unsaturated cyclic hydrocarbons.²⁶

The rate of hydrogenation of acrylic acid on Pt black at 298 K in an acoustic field (440 kHz, 5 W cm^{-2}) is three times as high as that under mechanical stirring at 1000 rpm (see Ref. 106). The use of ultrasound (1 MHz, 3 W cm^{-2}) in the catalytic hydrogenation of olive oil on Raney nickel made it possible to reduce appreciably the residual concentration of unsaturated compounds in the product (the iodine number was 77.0 after hydrogenation for 3 h and 50.0 after hydrogenation in the ultrasonic field).¹⁰⁷

Under the action of ultrasound, anthracene can be reduced by lithium to its dianion. Addition of water leads to the formation of 9,10-dihydroanthracene. Under similar conditions, diphenylacetylene yields a radical anion which then dimerises. This dianion may be captured by some species,⁵ as is shown in the scheme:



Ultrasonic waves speed up not only hydrogenation, but also dehydrogenation, which seems to be due to the fact that both reactions occur by the same mechanism. For example, the degree of dehydrogenation of tetrahydronaphthalene to naphthalene in the presence of 3% Pd/C as a catalyst in diethylene glycol at 473 K reaches 55% after 6 h.¹⁰⁸ The use of ultrasound makes it possible to decrease the temperature to 453 K and to achieve the total conversion within the same time. The use of pulse ultrasound is as effective as continuous ultrasound. Dehydrogenation of triethylene glycol in dimethyl ether is much less sensitive to ultrasound.

Ultrasound makes it possible to increase the efficiency of the preparation of deuterium-labelled compounds.¹⁰⁹ The Raney nickel-catalysed hydrogen exchange for deuterium in a monosaccharide was performed in different solvents under the action of ultrasound. Deuterium was introduced with a high stereospecificity and regioselectivity.

Ultrasonication of a reaction mixture containing barium hydroxide increased the rates of the reactions and the yields of products involving aromatic aldehydes. For example, 4-chlorobenzaldehyde does not enter into the Cannizzaro reaction in the absence of ultrasound. The use of catalytic poisons which affect selectively the oxidative active centres made it possible to establish that this reaction occurs on the reduction centres, the catalytic cycle being initiated by a single-electron transfer from the catalyst to the substrate.⁵

Acceleration of the aldol condensation of ketones in an ultrasonic field in the presence of Al_2O_3 is confirmed by the following data:¹¹⁰ sonolysis of 1-tetralone in an argon atmosphere at 353 K for 24 h produces the hydroxy ketone in 80%–90% yield, whereas in the absence of ultrasound its yield is not more than 52% after 144 h.

The rate of the Ullmann coupling of 2-iodonitrobenzene in dimethylformamide in the presence of copper bronze at 333 K is increased 64-fold upon sonication.¹¹¹ If this process is performed in the usual manner, but using the pre-sonicated copper bronze, its rate also increases compared to the reaction rate on the ultrasound-nontreated copper bronze, though to a much lesser extent. This effect may be easily explained by the decrease in the size of metal powder particles under ultrasonic treatment. An appreciable acceleration of the reaction under the direct action of ultrasound results from the constant activation of the metal surface. In addition, the sonochemical process has two other advantages: it requires a considerably smaller excess of copper and excludes sticking of metal powder to the walls of the reaction vessel.

Sonication was also employed in the synthesis of α -amino acids using amino acid γ -anion equivalents.¹¹² The reaction of

[†] Unfortunately, the mechanism of catalytic synthesis of NH_3 in an ultrasonic field is not considered in the relevant literature; therefore, only some suggestions may be discussed.

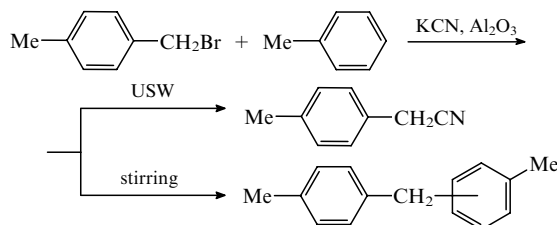
activated zinc with a iodohomoalanine derivative yields alkylzinc iodide, which reacts in the presence of palladium catalysts with a number of electrophiles (aryl iodides and acid chlorides) producing the corresponding α -amino acid derivatives. Sufficiently high yields are obtained using tetrahydrofuran as the solvent in the former case; to reach high yields in the reactions with acid chlorides under the action of ultrasound, it is necessary to use a combination of toluene and dimethylacetamide. Furthermore, alkylzinc iodide may be transformed into a zinc–copper couple, which reacts with allyl halides and reactive acid chlorides to give sufficiently high yields of the corresponding adducts.

The accelerating effect of ultrasonic treatment was exemplified in the liquid-phase alkylation of benzene by cyclohexene yielding cyclohexylbenzene.¹¹³ The reaction was conducted on an AlCl_3 catalyst prepared by the method of chemical deposition on SiO_2 from the vapour phase. These catalysts are active below 273 K and can be regenerated. Despite the fact that the activity of the catalysts becomes lower in successive experiments, they can be used repeatedly. At least until the sixth cycle, the turnover number was 110. Apparently, reactions on solid catalysts are limited by the diffusion of reagents and/or products into the catalyst's pores. The ultrasonic impact in the course of catalytic reaction provides an accelerating effect, so that, depending on the size of the catalyst's particles, the reaction rate can increase by even one order of magnitude.

It is of note that the action of surface acoustic waves changes appreciably the activation energy and the reaction orders on oxidised catalytic surfaces, whereas on the reduced surfaces these changes prove to be much smaller. At a resonance frequency, oxidation of ethanol on palladium is accelerated 140–160 times, which may be explained by a stronger distortion of the lattice under these conditions.⁷²

The application of USW speeds up substantially β -hydroxylation of acrylonitrile at room temperature (the same effect was also revealed in a homogeneous reaction¹⁰¹) on a catalytic system comprising copper(I) oxide and tetramethylethylenediamine. With the use of USW, the yield of the β -adduct also increases from 30% (stirring) to 70%–75%.¹¹⁴ Ultrasonic acceleration of reactions on non-metal catalysts (using HSiCl_3 as the silylation agent) was not studied as thoroughly as that on metals,^{115,116} nonetheless, in these cases too the increase in the reaction rate is related to the increase in the specific surface of the solid reagent due to the decrease in the particle size upon cavitation and the improvement in the mass transfer of a liquid reagent to the solid phase surface.

The reaction route can also be changed under the action of ultrasound.⁵ Stirring aluminium oxide with KCN in a mixture of *p*-methylbenzyl bromide and toluene leads to the formation of products of the Friedel–Crafts reaction (in this case, aluminium oxide acts as a catalyst). Under the action of ultrasound, this reaction follows a different route: *p*-methylbenzyl cyanide is formed as a result of direct substitution of CN for Br.



The change in the composition of products upon sonication is presumed to be due to the saturation of the Lewis acid centres on the aluminium oxide surface with CN^- ions, which induces nucleophilic substitution.⁵

The reaction of aryl iodides with zinc powder accelerated by ultrasound yields arylzinc compounds which contain the electron-withdrawing groups, *viz.*, CO_2Me , $\text{C}(\text{O})\text{NMe}_2$, CN, Br, Cl and CF_3 . The presence of these groups provides fairly good yields of

asymmetric multifunctional biaryls in the catalytic synthesis with participation of $\text{Pd}(0)$.¹¹⁷

Ultrasonication is also employed in electrochemical processes for intensifying the electrode reactions, which may be exemplified in the sonovoltammetric reduction of nitrobenzene on glassy carbon and gold electrodes.¹¹⁸ The four-electron reduction of nitrobenzene in an alkaline solution (pH 13) was studied as a model. The mechanism of electrochemical reduction is known to be complex; it includes protonation and dehydration, the processes proceeding both on the surface and in bulk depending on the nature and the state of the electrode. In the absence and in the presence of ultrasound, the reduction of nitrobenzene on the glassy carbon electrodes includes a chemically reversible process followed by the irreversible three-electron reduction. The combined use of a rotating disc and sonovoltammetry permits one to decrease the capacity of the double layer.

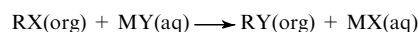
Electrochemical dehalogenation of organic compounds in microemulsions of a system didodecyldimethylammonium bromide–water–dodecane under the action of ultrasound in the presence of zinc phthalocyanine as a catalyst proceeds faster than in a homogeneous system including toxic and expensive organic solvents.¹¹⁹

Thus, ultrasound accelerates the heterogeneous catalytic reactions owing to a better mass transfer, smaller size of the surface particles and creation of active centres on which the substrate undergoes specific transformation.

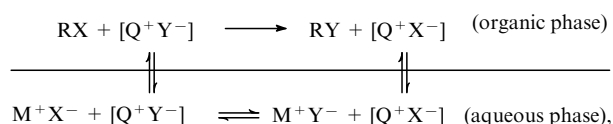
3. Phase-transfer catalysis

Ultrasound initiates and accelerates reactions in phase-transfer catalysis.^{120,121} The chemical effect of ultrasound in this case is also explained by the coalescence of cavitation bubbles, whereas its mechanical impact is associated with the formation of a highly dispersed emulsion which increases appreciably the interface area.

The mechanism of a typical phase-transfer reaction resembles the substitution mechanism. The overall equation

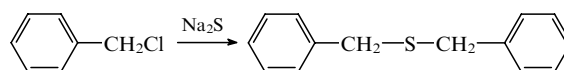


includes the catalytic cycle

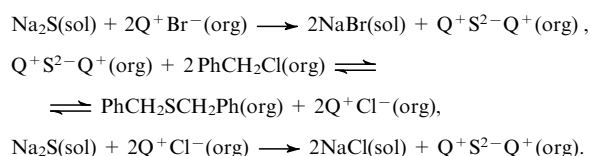


where Q^+ is the cation of the phase-transfer catalyst (PTC).

Combined action of PTC and ultrasound in heterogeneous reactions can be exemplified in the reaction of benzyl chloride with solid sodium sulfide in the presence of tetrabutylammonium bromide as PTC and acetonitrile as the solvent.¹²²



The proposed mechanism includes two phase-transfer ion-exchange stages and the main reaction in the organic phase:



The results obtained upon the use of PTC and ultrasound and upon their combined action are shown in Fig. 3.

The catalytic cycle of transformation of benzyl chloride includes the transfer of sulfide anions to the organic phase. The influence of ultrasound on the molecular diffusion and dissolution of sodium sulfide in acetonitrile is minimal, whereas a slight increase in the conversion occurs owing to the development of

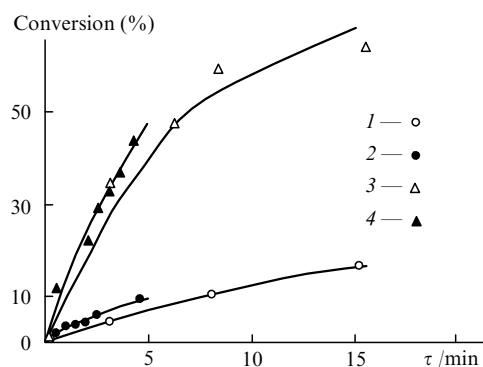


Figure 3. Results of the use of PTC and ultrasound in the reaction of benzyl sulfide formation (USW intensity, 150 W cm^{-2}): (1) without USW and PTC; (2) with USW; (3) 0.4% PTC; (4) 0.4% PTC + USW.

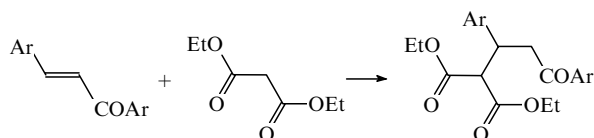
the interface where the reaction takes place, facilitation of mass transfer and effective stirring of the reagents as a result of cavitation. Combination of PTC and ultrasound gives a maximum increase in the conversion owing to the additive effect of their individual impacts on the system.

Ido *et al.*¹²³ investigated the possibility of the multiple use of phase-transfer catalysts. The catalyst (hexadecyltri-*n*-butylphosphonium bromide) is concentrated in the third phase formed between the organic (dodecane) and the aqueous (saturated KBr solution) phases. This interface catalyses substitution in benzyl chloride by bromide, the former being in the organic phase and the latter, in the aqueous phase. After completion of the reaction, the organic phase was removed and a new phase was introduced. The application of USW made it possible to avoid direct contact between the organic and the aqueous phase. The three phases were not mixed, the reagents were transferred across the interface under the impact of ultrasonic vibrations.

According to the theoretical concepts,⁴⁸ the chemical action of ultrasound is limited by the unpaired electron transfer. In this case, the reaction mechanism includes only ionic species; therefore, the effect of ultrasound is of physical nature. Ultrasound in fact increases the catalyst surface area since cavitation prevents agglomeration of particles.

Sonochemical acetylation of tertiary alkyl halides in the presence of zinc acetate was accomplished in the presence of PTC and under the action of ultrasound.¹²⁴ Alkylation of a glycine derivative by activated organohalogen compounds under the conditions of ultrasonic acceleration of phase transfer and subsequent hydrolysis of the products yielded aminoacylsultams and then, upon mild saponification, pure α -amino acids in a rather high overall yield.¹²⁵

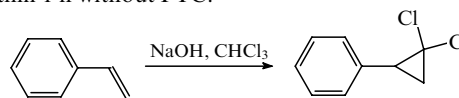
In the example of the addition of ethyl malonate to chalcone in the presence of KOH and trimethylbenzylammonium chloride as PTC (the Michael reaction) it was shown that with ultrasonic stirring the reaction is complete in 2 min, instead of 1 h.⁸⁹



Allylation and benzylation of sodium 5- β -D-glucopyranosyl-1,3-dimethylbarbiturate in water were carried out with benzyl bromide in Me_2SO or allylic and benzylic bromides in the presence of PTC under sonication.¹²⁶

The application of ultrasound in combination with phase-transfer catalysts, crown-ethers and lithium chloride accelerated the transformation of 6-methoxytetralins into 8-methoxytetralins including the stages of cleavage and cyclisation by the intermolecular Friedel–Crafts alkylation.¹²⁷

It is noteworthy that in many cases the application of ultrasound makes it possible to avoid PTC. An example is the cyclopropanation of styrene in which the yield of 96% was reached within 1 h without PTC.¹²⁸



In the control reaction carried out under mechanical mixing the yield was only 30% after 16 h.

4. Enzymic catalysis

Recent studies show the possibility of the ultrasonic influence on enzymic reactions. Acoustic vibrations increase substantially the activity and decrease the size of subtilisin particles which catalyse trans-esterification in organic solvents, the changes in the USW amplitude having no effect on the reaction rate.¹²⁹ It was shown that the activity of enzymes depends on the duration of sonication. Thus a short-term action of ultrasound activates butyryl cholinesterase, whereas a prolonged action brings about partial dissociation of the tetrameric enzyme and its irreversible inactivation.¹³⁰ Total inactivation of peroxidases (lipoxenases and phenol oxidases) under the action of ultrasound and elevated temperatures is used in food technologies.¹³¹

Ultrasound was shown to influence hydrolysis of sucrose catalysed by invertase.¹³² The effect of ultrasound was studied over a wide range of changes in biochemical and physical conditions, such as pH, sucrose concentration and USW intensity. It was found that the reaction rate increases at low sucrose concentrations. At high concentrations, continuous ultrasonic vibrations have a more substantial influence on this enzymic reaction.

The rate of reactions catalysed by lipase from porcine pancreas is increased 3–60 times under the conditions of azeotropic distillation and 7–83 times under the action of ultrasound, the enantioselectivity being preserved in both cases.^{133, 134}

IV. Regeneration of catalysts

Traditional techniques for the regeneration of catalysts include their high-temperature calcination in the atmosphere of oxygen to remove organic residues.¹³⁵ However, the initial catalyst's activity is not recovered completely. The physical components of the ultrasonic action make it possible to use acoustic treatment for the effective regeneration of catalysts. Thus the initial activity of a brass catalyst used for the preparation of acetone from propan-2-ol recovered to 83% under the action of ultrasound (18–22 kHz, 6–20 W cm^{-2}) in a solution of sulfuric and nitric acids and sodium bichromate.⁵ Without ultrasound, the activity of this catalyst recovered only to 63%.

Ultrasound intensifies considerably the oxidative regeneration of the deactivated rhodium triphenylphosphine catalyst used in the hydroformylation of alkenes.¹³⁶

A nickel-molybdenum catalyst used for the cracking of hydrocarbons was regenerated by oxidation in air with the subsequent action of USW in low-viscosity oils.⁵ Similarly, a 30-min action of an acoustic field in water led to the regeneration of the activity of a catalyst of denitrification of waste gases (TiO_2 – V_2O_5).

Ultrasound restores totally the specific surface, porosity and activity of the palladium–aluminium catalyst APK-Z, which is used for the removal of nitrogen oxides from exhaust gases.¹³⁷ The activity of the 3% Pd/C catalyst in diethylene glycol used for the dehydrogenation of tetrahydronaphthalene and studied earlier in an analogous reaction without ultrasound¹³⁸ decreases in the course of the reaction, but it can be restored with the aid of ultrasound.¹⁰⁸

A series of studies^{24, 139–143} were devoted to the regeneration of the industrial ShPAK-0.5 catalyst (0.5% Pd/ Al_2O_3) modified by zinc acetate, pyridine and KOH. This catalyst is used for the selective hydrogenation of the triple bond of acetylenic alcohols to

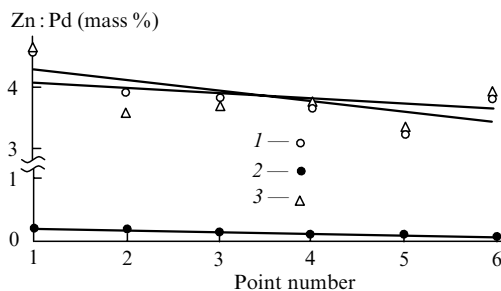


Figure 4. Changes in the Zn:Pt ratio across the granule in subsurface layers of a fresh catalyst (1), exhausted catalyst (2) and a catalyst following sonication (3). The distance between the points is 0.05 mm.

the double bond in the synthesis of vitamin A and E intermediates. In the course of hydrogenation, the catalyst loses its activity and its selectivity is decreased. Besides, the use of physicochemical methods (X-ray spectral microanalysis, electron microscopy and X-ray photoelectron spectroscopy) showed that the catalyst's surface is changed substantially. The ultrasonic treatment with an intensity of 1 W cm^{-2} and a 3-min duration leads to the total recovery of the initial properties of the catalyst (Fig. 4).⁵⁴ After the ultrasonic treatment, the content of zinc and palladium in the surface layers of the regenerated catalysts becomes the same as that in the fresh sample. Probably, this is explained by the purification of the surface from coke deposits and the diffusion of the zinc atoms into the subsurface layer. The XPS data also point to a possible amorphisation of the structure of the catalyst's surface, which is at variance with the conclusions made in Refs 54 and 66.

V. Conclusion

The application of ultrasound in chemistry, particularly in catalysis, is one of the most fortunate examples of the use of non-conventional physical methods influencing a reaction system. The present review reflects only the basic results of studies of the applicability of USW for the preparation, activation and regeneration of various catalytic systems as well as for conducting catalytic reactions. The unique results of the action of ultrasound make rather attractive the prospects of its technological uses and are also of appreciable interest for fundamental research. Summing up the above considerations, let us emphasise the following most important moments.

It has been established that ultrasound increases the specific catalyst's surface, because cavitation prevents the agglomeration of particles. The action of ultrasound on solids, including catalysts, increases the content of small particles (3–5 nm) and modifies their lyophilicity. Under ultrasonic treatment, the increase in the activity of catalysts is often several orders of magnitude larger than the increase in their specific surface. This may be associated with a specific action of ultrasound on the nature of the active centres. The change in the nature of the active centres influences not only the catalytic activity but also the reaction selectivity, including enantioselectivity. In an ultrasonic field, the rate of catalytic reactions remains constant for a long time, i.e., the stability of a catalyst is enhanced. In addition, the acoustic waves can change the activation energy and the reaction orders. The combined use of phase-transfer catalysts and ultrasound provides a maximum increase in the degree of conversion owing to the addition of their individual impacts on the system. In a number of cases, the application of ultrasound makes it possible to conduct reactions without phase-transfer catalysts.

A topical problem is the use of USW and resonance vibrations for the creation of heterogeneous catalysts with adjustable functions. Heterogeneous reactions in a liquid phase are limited by the diffusion of the reagents and/or the product in the catalyst's pores.

The application of ultrasonic vibrations in the course of a catalytic reaction leads to a several-fold increase in its rate depending on the size of the catalyst particles.

The optimum USW parameters are individual for each catalyst and catalytic reaction. The ultrasonic treatment increases appreciably the spillover of hydrogen which explains higher activity of ultrasound-treated catalysts in hydrogenation reactions. The phenomenon of catalyst's deactivation, which is sometimes observed at a longer duration and a higher intensity of ultrasonic treatment, may be explained by the rearrangement of active centres, which is in turn related to the modification of the catalyst's surface.

The fundamental question about a detailed mechanism of catalysis in an ultrasonic field remains still open to debate. Solution of this problem is a priority issue in the catalysis and determines the prospects of the technological use of USW.

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^e — *Russ. Chem. Bull. (Engl. Transl.)*

Heat-accumulating properties of melts

A M Gasanaliev, B Yu Gamataeva

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Abstract. Data on the heat-accumulating properties of melts are generalised. The principles and methods of thermal energy accumulation with the use of melts are considered. The problem of search for heat-accumulating materials with the required properties based on multi-component systems of anhydrous inorganic compounds is discussed. The bibliography includes 57 references.

I. Introduction

One of the major problems of the national economy, *viz.*, decreasing power consumption of production, can be solved by two methods. The first one is more efficient transformation of primary energy into electrical and thermal energy. This can be done by increasing the efficiency factor of power stations, by using cheaper fuel types or renewable energy sources, such as wind, geothermal sources, tides, sea waves, *etc.*

The second method of ever-growing importance involves increasing the efficiency of the energy utilisation by the consumer. The expenses for saving fuel and electric power are two to three times lower than those required for expanding the fuel and energy base. The following measures for improving the efficiency of energy usage by the consumers can be listed: transition to more perfect and less power-consuming technologies; use of secondary power resources; smoothing the time differences between the energy generation and energy demand schedules by means of accumulation.

Accumulation of electric energy is a difficult problem. The capacities of the existing electrochemical accumulators are insufficient for their use on an industrial scale. The promising superconducting electric power accumulators are still under development. The hydraulic methods for energy storage make it possible to accumulate significant amounts of energy; however, this involves large capital investment and impact on the environment (not always favourable).

Methods for the thermal energy accumulation have been developed in detail and tested under various conditions. The world energy crisis of the 1970s has confirmed once again the

urgency of the problem of the thermal energy accumulation followed by heat recovery and transformation into useful work.¹

Studies along these lines include two aspects, namely, the chemical-technological and technical-physical ones.^{2,3} The chemical-technological aspect includes choosing the heat-accumulating materials (HAM), studying their properties and selecting the accumulation method. The thermal energy accumulation and recovery methods involving melts are based on the following processes: heating compounds to a high temperature followed by heat release on cooling (heat accumulation due to the heat capacity of the solid and liquid phases); reversible first-order phase transitions (accumulation due to latent heat of phase transitions); reversible chemical reactions (chemical accumulation). The technical-physical aspect examines selection of the processes for the transformation and use of the stored energy.

National programmes on the thermal energy accumulation with the use of reliable and inexpensive accumulators have been developed in different countries and are now being implemented. The use of such accumulators enables one to replace the traditional fuel types (coal, natural gas) by non-traditional renewable energy sources^{4,5} as well as allows one to use the spent heat in chemical-technological processes or for heat supply.

However, an important drawback of heat accumulators is the high cost of accumulated energy, mainly because of the cost of the HAM. For this reason, the development of heat accumulators starts from the search for cheap HAM with high heat capacity and predetermined properties.

Synthesis of novel inorganic materials with predetermined properties requires complex studies of fusibility diagrams and physicochemical properties of multi-component systems by modern physicochemical methods, primarily those using computer 3D simulation methods.^{2,6–8}

Recent studies on HAM mostly deal with crystal hydrates of inorganic salts, salt eutectics and metal alloys traditionally used in this field. The present review generalises the data regarding the methods and principles of the thermal energy accumulation using melts of anhydrous inorganic compounds as the HAM. Criteria for the estimation of the heat-accumulating ability of melts and a new methodological approach to the development of HAM based on multi-component systems and study of their physicochemical properties are considered. Special attention is given to the systematisation of experimental data on the fusibility diagrams of multi-component systems.

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II. Methods of the thermal energy accumulation with the use of melts

The most popular heat accumulators use melts as the HAM. They can accumulate thermal energy either due to the heat capacity of solid or liquid media or due to the latent heat of phase transitions and chemical reactions. Non-isothermal and isothermal accumulators are distinguished, depending on the mode of heat storage.

1. Heat accumulation due to the heat capacity of solid and liquid media

The most popular method of heat accumulation is that due to the heat capacity of liquid and solid media. A compound which accumulates heat due to the heat capacity of its different phases is called a heat-capacity compound. Heat accumulators with such a compound as the working medium are non-isothermal. They are used for the heat accumulation over a broad temperature range (several hundred degrees). The allowed temperature variation in an accumulator is normally specified (it is determined by the temperature of the heat source, the temperature of the heat-carrier, the temperature required by the consumer, and the temperature differences controlling the intensity of heat exchange during the accumulator charge and discharge phases). Water (for temperatures up to 100 °C), air, noble gases, melts of simple and complex inorganic compounds and technical oils can serve as heat-carriers.

If melts are used as heat-capacity HAM, it has to be taken into account that the specific heat is generally independent of temperature and is a constant. The specific energy stored by a heat-capacity heat accumulator is determined by the formula

$$Q = C_p \Delta T,$$

where C_p is the specific heat of the accumulator working medium at constant pressure; ΔT is the difference between the starting and final accumulation temperatures.

It is known from thermodynamics that the specific heat is the higher the smaller the relative molecular mass of the compound. Therefore, compounds with small molecular masses are used as working media for heat-capacity accumulators.

Of anhydrous inorganic compounds, systems based on oxides, the so-called refractory compounds, are used as the HAM most commonly. The properties of the most promising oxide-based HAM are analysed in Ref. 9. A great many experimental studies relate to the determination of the dependences of C_p , thermal conductivity factor (λ) and apparent density (ρ) on temperature and open porosity (O_p). In some cases, natural minerals and anhydrous inorganic compounds obtained from them are used, *e.g.* granite, sand, pebbles, gravel, cobble-stone, macadam, sand-pebble mixture, *etc.* Such heat-capacity HAM are inexpensive and readily accessible, are not corrosive with respect to construction materials, but have low effectiveness in terms of their thermal properties, which results in the low density of the accumulated energy.

The increase in the specific density of the heat-capacity HAM increases the specific heat, and hence the amount of accumulated heat in the bulk material. The materials based on magnesia have the highest heat capacity; these materials have sufficient thermal

conductivity in the temperature range 100–900 °C to be used as heat-capacity HAM (Table 1).

As the proportion of magnesia and the material apparent density increase, the thermal conductivity increases. The thermal conductivity of hyperdense heat-capacity HAM (3.55–3.97 kg m⁻³) exceeds 30 W m⁻¹ K⁻¹ at 100 °C, while it is less than 5 W m⁻¹ K⁻¹ for dense (3.00–3.50 kg m⁻³) and medium-density ones (1.83–2.96 kg m⁻³).⁹ Medium-density materials containing mixtures of magnesia with SiO₂, Al₂O₃, Cr₂O₃, or CaO and having an open porosity of 20%–30% are most efficient in terms of thermal conductivity (λ changes from 0.74–3.93 at 100 °C to 1.07–1.80 at 900 °C). Magnesia-based materials containing chromium oxide are the most heat-resistant (see Table 1).

2. Heat accumulation owing to the latent heat of phase transitions

The accumulation of heat with the use of the latent heat of phase transitions of anhydrous inorganic compounds is possible in the following changes in the state of aggregation:^{3,8} melting $\rightleftharpoons$ crystallisation, vapourisation $\rightleftharpoons$ condensation, sublimation and decomposition.

The heat-accumulating materials which accumulate heat due to phase transitions are called phase-transition HAM. The accumulators with such materials as the working media are isothermal.

The accumulators in which the latent heat of the melting $\rightleftharpoons$ crystallisation phase transition is used have good energetic characteristics. The principle of such an accumulator is based on the thermal energy absorption accompanying the crystal lattice destruction upon heating of a compound and energy liberation upon crystallisation of the melt on cooling.

In many technological processes, the only useful thermal energy is that accumulated due to the heat of phase transitions and due to the heat capacity of the material in the liquid phase.^{10–14} These processes include: maintaining the given operating temperature of steam at thermal and nuclear power plants; transformation of thermal energy into electrical energy through the Brighton cycle; thermal energy accumulation and transfer with the use of molten phase-transition HAM as heat-carriers; increasing the efficiency of non-traditional systems by compensating for the intermittent and non-steady nature of renewable energy sources (solar, wind, geothermal, *etc.*).

The type of the thermodynamic cycle and the nature of the HAM are determined by the operating temperature range of the heat accumulator. This primarily assumes a relationship between the characteristics of the main power system, the accumulator and the parameters of the cycle in which the mass and heat transfer occur. For example, Table 2 lists the efficiency values of three cycles. Yet another example: the maximum temperature of the hot source at a solar power station without radiation concentrating by local concentrators is about 100 °C. In this case, it is only possible to speak about a cycle with evaporation of the working media such as freons. However, these working media cause ecological problems if they leak. In this case, a perfect HAM would consist of eutectic compositions based on *n*-component mixtures of hydrates and anhydrous compounds with m.p. $\leq$ 100 °C.

The thermal characteristics of the most promising systems based on aluminium chloride and alkali metals with the heat-accumulating ability above 0.3 GJ m⁻³ are presented in Table 3.

Table 1. Heat-accumulating properties of oxide heat-capacity HAM in the temperature range 100–900 °C.

Refractory compounds (mass %)	O_p (%)	ρ /kg m ⁻³	C_p /MJ m ⁻³ K ⁻¹	λ /W m ⁻¹ K ⁻¹
Chamotte, 28 $\leq$ Al ₂ O ₃ $\leq$ 45	20–24	2.05–1.85	1.5874–2.4232	0.74–1.07
Periclase-chromite, 65.5 MgO–14.2 Cr ₂ O ₃	24–30	2.81–2.52	2.3575–3.5011	2.42–2.08
Forsterite, 58.3 MgO–38.9 SiO ₂	20–30	2.69–2.29	2.2115–3.5409	3.93–1.80
Periclase-spinel, 75.6 MgO–18.2 Al ₂ O ₃	3–10	3.15	3.1617–4.0219	2.04–3.33
Periclase	0–3	3.55–3.37	3.6954–4.5683	34.82–7.52
Magnesian limestone, 70 MgO–26.2 CaO	18–21	2.80–2.68	3.2217–3.4232	1.74–2.72

Table 2. Characteristics of thermodynamic cycles.

Cycle	Characteristic cycle parameter	Efficiency
Temperature range 40–268 °C		
Carnot	–	0.420
Rankin	steam under a pressure of 5 MPa	0.365
Temperature range 40–450 °C		
Chirn	evaporation at 268 °C	0.380
Carnot	–	0.567

Table 3. Characteristics of phase-transition HAM for accumulation of low-potential thermal energy (m.p. ≤ 100 °C).

System (mass %)	M.p. /°C	ρ /kg m ⁻³	ΔH_m (see ^a)	
			I	II
77 AlCl ₃ –5 BaCl ₂ –18 NaCl	50	1786	168.5	0.3009
88.5 AlCl ₃ –11.5 LiCl	80	1645	199	0.3274
22.2 LiNO ₃ –10.9 NaNO ₃ –66.9 NH ₄ NO ₃	81	–	127	–
26.4 LiNO ₃ –58.7 NH ₄ NO ₃ –14.9 KNO ₃	81.5	–	–	0.234
78.1 AlCl ₃ –5.5 KCl–16.4 LiCl	85	1631	196	0.3207
77.9 AlCl ₃ –11.3 KCl–10.8 NaCl	88	1653	191	0.3185
73.8 AlCl ₃ –21.8 NaCl–4.4 TiCl ₃	98	1659	192	0.3185
73.7 AlCl ₃ –22.2 KCl–4.1 TiCl ₃	100	1650	184.2	0.3039
63.8 AlCl ₃ –18.1 KCl–18.1 TiCl ₃	100	1743	156.1	0.2756

^a The accumulated energy is usually expressed as enthalpy/weight ratio $\Delta H/M$ or enthalpy/volume ratio $\Delta H/V$, therefore the dimensionalities are: (I) kJ kg⁻¹; (II) GJ m⁻³.

Judging by the data listed, the choice of phase-transition HAM for the accumulation of low-potential thermal energy is limited, particularly if one takes the cost of the accumulated energy into account.⁷

Studies of movement of the solidification (melting) frontier of HAM on a planar unit cell model of a heat accumulator¹⁵ were carried out using an eutectic three-metal alloy with composition (mass %) 50 Bi–31 Pb–19 Sn and the parameters: $T = 94.5$ °C, $\rho = 9590$ kg m⁻³, $\Delta H_m = 26.4$ kJ kg⁻¹, $C_p = 0.138$ kJ kg⁻¹ K⁻¹, $\lambda = 16.5$ W m⁻¹ K⁻¹ as a phase-transfer heat-accumulating material.

The heat-accumulating ability of metal alloys (> 0.2 GJ m⁻³) is ensured by their high densities, unlike the case of salt melts where this ability is ensured by the enthalpy of melting (see Table 3).

It has been shown (see, *e.g.*, Refs 8 and 16) that an efficient short-term accumulator of average-potential thermal energy can be represented by an accumulator that uses the heat of phase transitions (melting $\rightleftharpoons$ crystallisation) of mixtures of anhydrous inorganic compounds. These mixtures represent mainly n -component eutectic compositions of molten alkaline and alkaline-earth metal salts with melting points of 100–500 °C. The ranges of the melting points (m.p.) and ΔH_m for the recommended phase-transition HAM and the most promising eutectic compositions are given in Table 4.

Thermodynamic analysis of such systems shows^{8,19} that the highest heat-accumulating ability is characteristic of salt eutectics based on lithium nitrate possessing high heats of phase transition (370 kJ kg⁻¹) and thermal stability up to 500 °C and a melting point of 256 °C; in addition, these are not corrosive with respect to many structural materials and their alloys. Eutectic compositions containing only alkali and alkaline-earth metal nitrates (except for LiNO₃) can be used at operating temperatures only 30–50 °C higher than their melting points (due to decomposition).

Table 4. Characteristics of phase-transition HAM for accumulation of medium-potential (100 < m.p. < 500 °C) thermal energy.^{6,16–18}

System (mass %)	M.p. /°C	ρ /kg m ⁻³	ΔH_m (see ^a)	
			I	II
29 LiNO ₃ –17 NaNO ₃ – –49.4 KNO ₃ –4.6 Sr(NO ₃) ₂	105	2087	110	229.6
17.5 LiCl–82.5 AlCl ₃	114	2376	251	596
21.6 KCl–78.4 AlCl ₃	128	2343	254	595
31.7 LiNO ₃ –68.3 KNO ₃	135	1780	135.6	241.4
55.4 LiNO ₃ –4.5 NaNO ₃ – –40.1 KCl	160	1905	266	507
58.1 LiNO ₃ –41.9 KCl	166	1918	272	522
47.9 LiNO ₃ –1.4 LiCl– –50.7 NaNO ₃	180	1986	267	530
57 LiNO ₃ –43 NaNO ₃	193	1880	248.3	467
45 LiNO ₃ –47 NaNO ₃ – –8 Sr(NO ₃) ₂	200	1993	199	397
87 LiNO ₃ –13 NaCl	208	1889	369	697
93.6 LiNO ₃ –6.4 NaCl	220	1850	363	675
98 LiNO ₃ –2 Li ₂ SO ₄	255	2357	354	834.4
1.8 LiF–39.9 LiCl– –8.3 NaCl–50 KCl	368	2048	523	1071
29 LiCl–24 LiF– –21 Li ₂ CO ₃ –26 Li ₂ SO ₄	419	2252	387	871.4
29.6 KCl–53.8 Li ₂ SO ₄ – –16.6 NaCl	420	2062	586.2	1209
26.9 NaCl–73.1 Sr(NO ₃) ₂	424	2152	244	252

^a The dimensionalities are: (I) kJ kg⁻¹; (II) MJ m⁻³.

High ΔH_m values are characteristic of alkali metal chlorides and sulfates, and hence intense heat liberation is observed on the DTA (or DSK) cooling curves for eutectic mixtures with lithium nitrate.¹⁶ Addition of alkali metal nitrates to halide-, sulfate- and carbonate-containing mixtures of alkali and alkaline-earth metals allows not only reduction of the operating temperature but also an increase in the heat-accumulating ability, as well as a decrease in the corrosive effect of these mixtures on structural materials.

The number of components in promising eutectic systems (n) ranges from 1 to 4. If $n > 4$, degeneration with respect to both the melting points and the physicochemical properties occurs; this increases the cost of the accumulated energy with the heat-accumulating ability being the same.

Technical and economic analysis showed that accumulators with high-temperature phase-transition HAM (m.p. > 500 °C) as the heat-carriers, particularly eutectic compositions of salt and metal multi-component systems, are most suitable for non-traditional energy sources.⁵ However, the development of such accumulators entails the solution of a number of complex technical problems (for example, the corrosion compatibility of the HAM with structural materials, intensification of heat exchange in the charge and discharge modes, regeneration of the HAM, *etc.*).

Of the phase-transition HAM used for the thermal energy accumulation, eutectic metal alloys possess the best thermal conductivities and stabilities. Analysis of published data on thermodynamic parameters of metal-based multi-component systems^{17,19} made it possible to single out the most promising ones for use as the working materials in heat accumulators (Table 5).

Of ionic compounds, alkali and alkaline-earth metal fluorides, chlorides, carbonates, and sulfates have the best thermal properties for the accumulation of high-potential thermal energy. Salt eutectics are the most power-intensive (due to the enthalpy of melting, see Table 6). The ΔH_m values were found experimentally or calculated using the additivity principle. The experimental studies of heat capacity were carried out using a continuous-heating calorimeter.¹⁷

Table 5. The characteristics of phase-transition HAM from metal alloys.

System (mass %)	M.p. /°C	ρ /kg m ⁻³	ΔH_m (see ^a)	
			I	II
78.55 Ga–21.45 In	15.7	6197	69.7	0.4429
86.5 Ga–13.5 Sn	20.55	5885	81.9	0.4942
96.5 Ga–3.5 Zn	25.0	5946	88.5	0.5415
67 Ga–20.5 In–12.5 Zn	10.7	6170	67.2	0.4185
82 Ga–12 Sn–6 Zn	18.8	5961	86.5	0.5255
74 Ga–22 Sn–4 Cd	20.2	5983	75.2	0.4571
93 Ga–5 Zn–2 Cd	24.6	6020	85.03	0.5246
13.3 Sn–50 Bi–10 Sb–26.7 Pb	70	8974	45.8	0.412
46.3 Mg–53.7 Zn	340	4600	185	0.851
96 Zn–4 Al	381	6630	138	0.916
34.65 Mg–65.35 Al	497	2155	285	0.615
60.8 Al–33.2 Cu–6.0 Mg	506	3050	365	1.113
64.6 Al–5.2 Si–28 Cu–2.2 Mg	507	4400	374	1.644
68.5 Al–5.0 Si–26.5 Cu	525	2938	364	1.069
64.3 Al–34.0 Cu–1.7 Sb	545	4000	331	1.324
66.92 Al–33.08 Cu	548	3600	372	1.339
83.14 Al–11.7 Si–5.16 Mg	555	2500	485	1.213
87.76 Al–12.24 Si	557	2540	498	1.265
46.3Al–4.6 Si–49.1 Cu	571	5560	406	2.260
86.4 Al–9.4 Si–4.2 Sb	575	2700	471	1.272

^a The dimensionalities are: (I) kJ kg⁻¹; (II) GJ m⁻³.

Table 6. Enthalpy of melting of salt eutectics with m.p. > 500 °C.^{16, 17, 20, 21}

System (mass %)	M.p. /°C	ΔH_m /kJ m ⁻³
50 Li ₂ CO ₃ –50 K ₂ CO ₃	505	335
64.25 LiCl–35.75 Li ₂ CO ₃	510	339.7
56.4 Na ₂ SO ₄ –12.9 NaCl–30.7 KCl	528	410
56.7 Li ₂ SO ₄ –10.3 Na ₂ SO ₄ –33 KCl	536	514.6
26.2 LiF–73.8 Li ₂ SO ₄	540	348.9
64.5 LiCl–35.5 NaCl	556	414.5
25.7 LiF–36.5 NaF–10.6 MgF ₂ –27.2 CaF ₂	593	510
24.8 LiF–75.2 Li ₂ CO ₃	595	594.5
10.4 NaF–39.4 NaCl–50.2 KCl	602	370.3
32.6 LiF–50.4 NaF–17 MgF ₂	622	625
34.7 LiF–3.3 NaF–37.5 MgF ₂ –24.5 CaF ₂	651	470
48 LiF–52 NaF	652	711
24 LiF–76 NaCl	680	476.9
67 LiF–33 MgF ₂	746	708
46 LiF–54 MgF ₂	750	847
75 NaF–25 MgF ₂	832	649
31 NaF–69 MgF ₂	996	710
29.5 KF–70.5 MgF ₂	1006	770

From the viewpoint of thermal accumulation, salt systems have drawbacks such as rather low thermal conductivities and undesirable volume increase by 10%–30% upon melting; because of this, it is necessary to provide free volume for thermal expansion of the melt in the accumulators.

Prediction of the properties of ionic systems without experimental studies was carried out using the equation¹⁷

$$\Delta H_m = \Delta H_m^{\text{add}} + \Delta \Delta H_m,$$

where $\Delta H_m^{\text{add}} = \sum x_i \Delta H_{m,i}(T_e)$; x_i is the mole fraction of the i th component; $\Delta H_{m,i}(T_e)$ is the enthalpy of melting of the i th component referred to the temperature of the eutectic.

Comparison of the $\Delta \Delta H_m$ values and the enthalpy of mixing of melts ΔH_{mix} showed¹⁷ that

$$\Delta \Delta H_m = \Delta H_{\text{mix}}.$$

Eutectic mixtures containing salts of stable intersecting elements of mutual systems have the highest heat content.¹⁶ Several papers report on the finding of stable intersecting elements in three-, four- and five-component mutual systems and studying their heat-accumulating properties.^{20, 22}

3. Chemical accumulation

Chemical accumulation implies the energy accumulation and release by virtue of chemical reactions. The accumulated energy can be released as heat, electrical energy, light, or mechanical energy.

Depending on the type of the accumulated energy, one distinguishes thermochemical (energy is accumulated as heat) and electrochemical accumulators (energy is accumulated as electrical energy sometimes supplemented with some heat).

Both natural organic (coal, oil products, natural gas, *etc.*) and synthetic fuels (organic and inorganic) can serve as chemical accumulators. A special place among the compounds used as heat accumulators in thermochemical accumulators belongs to melts and alloys of naturally abundant compounds, such as metals, oxides, hydroxides, salts, *etc.* Simulation of the thermodynamics and thermochemistry of reactions involving these compounds facilitates essentially the selection of the HAM and the calculation of parameters of chemical accumulators.

The state-of-the-art in this field was considered in Ref. 8. Accumulation can be based on three main reaction types involving melts of inorganic compounds: (1) synthesis of complex coordination compounds,^{23–25} inclusion compounds²⁶ and ammonia complexes,^{27, 28} hydration of alkaline-earth metal oxides (CaO, MgO);^{29, 30} (2) decomposition of carbonates,³¹ sulfates,³² alkaline-earth metal hydroxides, ammonium hydrogensulfate (NH₄HSO₄),³³ metal hydrides;³⁴ (3) exchange decomposition in full conversion points in mutual multi-component systems formed by ionic melts of inorganic compounds (hydroxides, salts).⁴ Of interest are chemical reactions that involve ionic compounds³⁵ capable of reversible accumulation (Table 7).

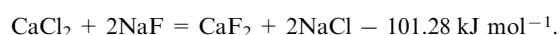
The following scheme of exchange reactions in mutual multi-component systems serves as the basis of heat accumulation:



where AX, BY, AY, and BX are ionic compounds; n , m , c , d are the stoichiometric factors in the exchange reaction; Q is the heat effect of the reaction.

This type of processes is also used for the synthesis of diverse compounds. For instance, exchange decomposition occurring to the full conversion point of ternary mutual system Na,Ca/F,Cl is, on the one hand, the most efficient method to obtain calcium fluoride; on the other hand, this is a process that can be used in thermochemical accumulators ($Q = 519.72 \text{ kJ mol}^{-1}$).³⁶

It is recommended to use a powder mixture of equivalent quantities of calcium chloride and sodium fluoride for reversible accumulation.³⁷ The thermochemical equation of the reaction is



The reaction starts at 490 °C. The mixture can be heated to a maximum temperature of 600 °C.

If the specific heat effect of the exchange reaction is within $30 \leq Q < 250 \text{ kJ kg}^{-1}$, accumulation of thermal energy is an efficient side process to save energy in chemical technology. If $Q > 250 \text{ kJ kg}^{-1}$, the reaction is applicable as a working process in thermochemical accumulators.

The major problem in the development of chemical heat accumulators is the choice of chemical reactions that meet the following requirements:³ the heat effects of the reaction should be

Table 7. Thermodynamic characteristics of some exchange decomposition reactions in ternary mutual systems.³⁵

Reaction	M.p. /K (see ^a)	$-\Delta H$ /kJ mol ⁻¹		$-\Delta G$ /kJ mol ⁻¹	
		ΔH_{298}°	ΔH_T	ΔG_{298}°	ΔG_T
2 NaOH + CaCl ₂ = 2 NaCl + Ca(OH) ₂	320	162.5	175.6	163.4	157.9
2 NaOH + CaSO ₄ = Na ₂ SO ₄ + Ca(OH) ₂	320	83.5	138.6	89.9	76.4
Na ₂ CO ₃ + CaCl ₂ = 2 NaCl + CaCO ₃	782	104.6	108.8	100.8	89.5
Na ₂ CO ₃ + Ca(NO ₃) ₂ = 2 NaNO ₃ + CaCO ₃	310	74.3	64.3	73.1	67.6
Na ₂ SO ₄ + CaCl ₂ = 2 NaCl + CaSO ₄	782	77.3	76.4	73.5	62.2
Na ₂ SO ₄ + Ca(NO ₃) ₂ = 2 NaNO ₃ + CaSO ₄	310	47.0	40.3	45.8	45.7
Na ₂ S + CaCl ₂ = 2 NaCl + CaS	782	138.6	141.5	136.5	124.7
Na ₂ S + CaSO ₄ = Na ₂ SO ₄ + CaS	890	61.3	65.1	62.6	59.6
2 (KOH + NaCl = KCl + NaOH)	320	53.3	55.9	43.7	31.1

^a The melting point of the lowest-melting reaction component.

no less than *ca.* 250 kJ kg⁻¹ or *ca.* 1800 kJ litre⁻¹ if gaseous products are taken into account; the volume density of the accumulated energy should be as high as possible at a minimum possible volume of the reaction products.

4. Comparative analysis of the properties of heat-accumulating materials

The prospects of the development of heat accumulators in which accumulation and liberation of energy occur due to the heat-accumulating properties of melts of inorganic compounds are estimated using the following HAM parameters: specific volume, heat capacity, heat and phase transition temperature (in chemical reactions, in solid and liquid phases).

The heat-capacity heat accumulators are less thermally efficient in comparison with phase-transfer and thermochemical ones, because the considerable 'heat storage capacities' needed despite the HAM temperature increase in them requires a minimum quantity of thermal energy consumed.¹ However, heat-capacity heat accumulators are characterised by low cost and simplicity and hence they have found wide use.

The accumulators with the use of the heat effects of reversible phase transitions are characterised by high energy density, small HAM mass and virtually constant operating temperature; the temperature difference of the heat-carrier transferring heat to the consumer and the heat source charging the accumulator is determined only by the required heat transfer intensity. In heat-capacity accumulators, in most cases this difference also depends on the change in the working medium temperature.

The drawback of the isothermal phase-transfer accumulators is that one has to use a different working medium with a specific phase transition (melting) temperature for each required temperature. In practice, phase-transfer heat accumulation is partially combined with accumulation of physical heat, *i.e.* with heat-capacity accumulation. These are called hybrid accumulators; they are most popular for high-temperature short-term accumulation.²⁰

The thermochemical heat accumulators ensure the compactness of the accumulator for long-term heat storage and the absence of losses, as well as the possibility of accumulation at ambient temperature without recourse to thermal insulation. However, the limited number of cheap chemical compounds that meet the requirements for HAM is the main obstacle for the development of such accumulators.³⁸

Comparative analysis shows that phase-transition HAM accumulate an order of magnitude more heat than materials that do not undergo phase transitions. This stems from the fact that the phase transition enthalpies of many compounds are much higher than the heat-capacity effect, particularly upon accumulation of medium- and low-potential thermal energy where the operating temperature range is not very wide. The evaporating and sublimating HAM accumulate 3–5 times more heat than the melting

ones, while the HAM in thermochemical accumulators accumulate an order of magnitude more than the evaporating ones.¹⁸

The basic obstacles preventing the wide use of heat accumulators include insufficient development of problems regarding good thermal insulation from the environment, the absence of well-developed models for the calculation of heat and mass transfer in heterogeneous systems and for increasing the efficiency of electric power reproduction and accumulator power rating. In view of this, studies of the thermal, thermodynamic and technological characteristics of the available HAM as well as development of novel power-intensive materials with a wide operating temperature range are required. Solution of the above problems would ensure the effectiveness, high performance and low cost of energy accumulation. The hybrid (phase-transition and thermochemical) heat accumulators with melts of inorganic compounds as the HAM can prove to be the most promising for the development of durable heat-accumulating systems. The increase in the efficiency of power system can amount from 15%–25% (with heat-capacity accumulators) to 80%–85% (with thermochemical accumulators); in these cases, the cost of the heat accumulator is about 5% of the total power system cost.³⁹

For each power system, the choice of particular methods for the thermal energy accumulation is determined by both local conditions and the results of actual technical and economic calculations.

III. Criteria for the estimation of the heat-accumulating properties of melts

When choosing the accumulator type, one has to consider such factors as the methods for the supply and removal of energy, the amount of the stored energy, the operating temperature levels, the storage period, the heat transfer intensity, the investment and working costs, and the requirements for operational reliability and safety.

In the design of a heat accumulator, the prime thing is the search for a HAM the properties of which affect the majority of the above-mentioned factors. The choice of the material is primarily determined by the operating temperature level and the amount of the thermal energy to be accumulated. The basic requirements for the melts which can be used as the HAM are as follows: an acceptable melting point determining the accumulator operating temperature; high values of such specific quantities as the heat effect (which eventually determines the volume of the material used, and hence, the accumulator compactness and cost), the heat capacity, the thermal conductivity, the density; low viscosity in liquid phase and low thermal expansion coefficient; stability of the physicochemical parameters in the operating temperature range, *i.e.* the absence of chemical transformations; stability of the thermal and thermodynamic characteristics of the HAM; low vapour density; abundance in nature; low cost.^{2, 17}

There are also a number of operational requirements for melts, such as operating safety (the absence of explosion hazard or the presence of gaseous products easy to detect, environmental safety, the absence of hazardous pollution), easy heat absorption and liberation (the absence of supercooling and segregation), stability of physicochemical properties in multiple duty cycles, low corrosivity toward structural materials.

The performance of accumulators employing melts of inorganic compounds as the phase-transition HAM much depends on the extent of their supercooling (below the phase transition temperature) and on whether phase stratification occurs. In order that the heat of phase transition are used more completely, it is necessary to ensure minimum overcooling when the HAM crystallises.¹ This means that liberation of the accumulated energy occurs at a lower temperature than the HAM melting point; as a result, the accumulator may fail to operate at this temperature. Therefore, one of the major requirements for phase-transition HAM is that they should have an equilibrium crystallisation point where the fluid phase is transformed into solid one, avoiding a metastable supercooled state. This requires creating conditions where crystallisation occurs quickly, for example, by using an additive that accelerates this process.⁴⁰ Supercooling in the crystallisation is a minimum if the difference between the HAM melting points and the heat source temperature is 5–10 °C. This temperature range makes it possible to reduce thermal losses and the extent of supercooling of the melt; on the other hand, it is sufficient to provide good heat transfer when withdrawing heat from the HAM. If the supercooling of the melt is 5–10 °C, heat dissipation virtually stops, hence increasing the crystallisation rate is of importance.

Of anhydrous inorganic compounds that can be utilised for heat accumulation, only certain chlorides and nitrates (*e.g.*, calcium chloride and nitrate) and eutectic compositions containing more than 40 mass % of these compounds crystallise with supercooling. Borax, sodium silicate, and strontium and barium fluorides and chlorides can be used as the crystallisation stabilisers.

Segregation decreases the heat exchange between the solid and liquid phases, which necessitates continuous stirring of the HAM during crystallisation.¹⁷

When designing heat-accumulating systems, a comprehensive approach is required, including the development of a procedure for numerical solution of multi-parameter heat exchange problems with the use of thermodynamic analysis methods, theoretical and experimental simulation for optimisation and studies of the thermal and thermodynamic properties of HAM and operating parameters of the accumulators.

The final stage of studies involves the development of methods for optimisation of the design of heat-accumulating systems as regards the thermal and economic efficiencies and environmental safety.

IV. Principles for the development of heat-accumulating materials based on multi-component systems

Development of promising HAM calls for search for specific compounds or eutectic compositions that combine the above-mentioned properties in the optimum way. The search for such compounds is a complex problem, as certain properties can be combined in a material, while others cannot. Therefore, preliminary estimation of the thermal characteristics of the known HAM and the selection of physicochemical systems which can serve as a basis for creating new materials should be carried out with regard to the most important thermal accumulation parameters, such as temperature, specific enthalpy (heat capacity) and density.

Pure anhydrous inorganic compounds and their eutectic mixtures are promising as the HAM.²³ Unlike crystal hydrates, eutectic mixtures undergo melting and crystallisation at constant temperature, irrespective of the number of components. The search for eutectic compositions is carried out with the use of reference data bases on the physicochemical properties of compounds and the fusibility diagrams. The starting components of eutectics include metals, alkali and alkaline-earth metal oxides, hydroxides, nitrites, nitrates, halides, carbonates, sulfates and phosphates, which belong to traditional HAM, as well as transition metal compounds.

At present, the choice of compositions that meet the requirements for the HAM is limited, especially from the viewpoint of the accumulated energy cost. Therefore, directed development of HAM and study of their properties and technological characteristics are topics of current interest.⁴¹

Novel materials can be created using the results of studies of the phase diagrams and composition–property diagrams for various physicochemical systems as their theoretical base. The trend of an increase in the information output with minimisation of experiment is characteristic of modern research in the field of multi-component systems. This is achieved by using: (1) experiment planning with the use of modern rapid methods;⁴² (2) computer simulations with modern solid modelling methods;^{42–50} (3) development of fast methods and measuring instruments for studying the composition–property diagrams that require the use of automatic recording systems, systems for data collection and processing and those for controlling the experiment.^{51,52} The development of methods and measuring instruments that enable the study of a set of properties in one experiment improves not only the information output but also the quality of the experimental data, since the results of measuring the different properties refer to the same sample in the same state.^{53,54}

The above ways of optimisation in the study of the composition–property diagrams can be used independently of each other, but combining them is the most efficient. This is taken into account in the development of algorithms for computer programs required for the simulation and automation of the physicochemical analysis of multi-component systems.^{55–57}

Algorithmisation and programming imply the wide use of modern methods for the calculation, prediction and analysis, both for preliminary estimation of the physicochemical properties and composition–property diagrams and for subsequent processing of experimental data with the use of computer programs. Then the confirming experiments performed on the basis of complex methodology for the study of multi-component systems are minimised.⁴⁰

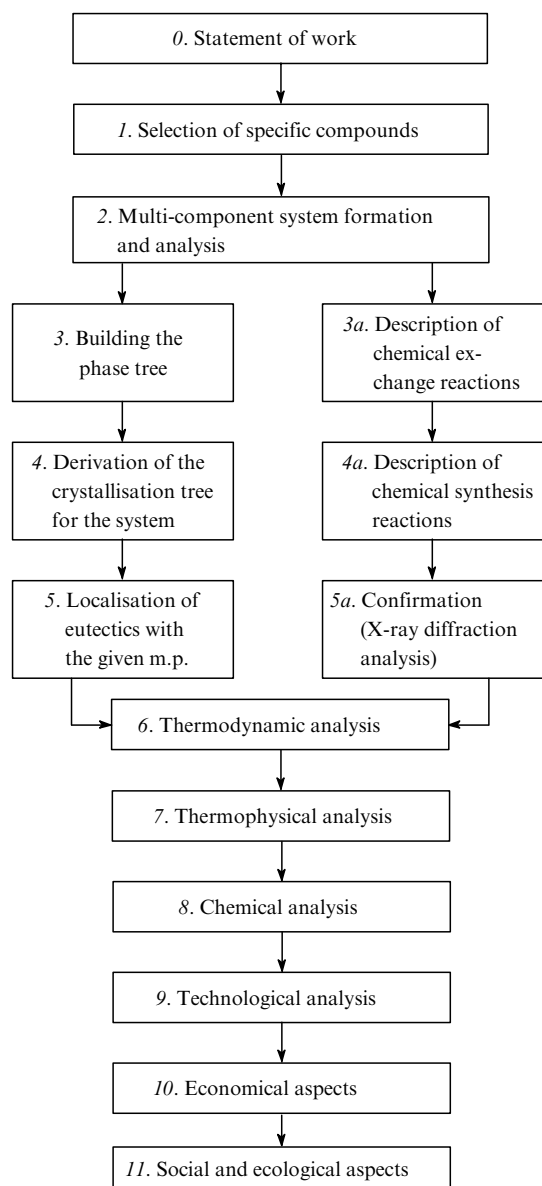
This approach allows one to establish the logical sequence of steps (from the choice of the starting components to the development of recommendations on the design of heat accumulators), to reduce the laboriousness of experimental studies, and to carry out directed, efficient and cost-effective choice of systems with pre-determined properties applicable as multi-purpose HAM.

A five-level algorithm has been suggested (Scheme 1) as a methodological basis for HAM development from melts² consisting of: zero level, statement of work (stage 0); first level, data analysis (stages 1 and 2); mathematical analysis level (stages 3 and 3a); experimental and theoretical level (stages 4–9); analytical level (stages 10 and 11).

The results of studies are presented graphically as the composition–property and property–property fusibility diagrams and in tabulated form.

The three basic rules should be observed in studies with the use of the algorithm suggested: (1) first, theoretical analysis as thorough as possible should be performed in each of the eleven stages; (2) a computer is used for work optimisation; (3) justified choice of compositions for subsequent studies is made in each level.

Scheme 1



V. Conclusion

Power plants used in various branches of industry are expensive, hence the increase in their efficiencies is a problem of vital importance. This problem can partially be solved by using accumulated energy. Presently, directed development and perfection of both heat accumulators and power-intensive working materials for them are under way.

The development of HAM implies not only the estimation of their chemical (corrosion activity), thermal (heat and mass transfer) properties and environmental safety but also the search for the optimum heat accumulator design with the use of simulation methods, calculation of its technical and cost efficiency and selection of structural materials.^{22–35}

The basic directions of chemical research on cost-effective HAM based on melts and their efficient operations include development of new and perfection of the existing methods of energy transformation and storage, search for new materials with controlled properties capable of serving as structural materials, heat accumulators and heat-carriers of heat accumulators, development of computerised methods for the simulation of the thermodynamics of heat and mass transfer in accumulators of particular design, optimisation of research and development efforts with the use of computers.

Depending on the required energy storage time period, buffer (15–60 min), short-term (up to 2–3 days) and long-term (week, month, season) accumulation types are distinguished. Accumulation of this duration is used in production of energy during 'peak hours' (hydroelectric, nuclear power plants), during cloudy hours (solar power plants), for supply of heat to stand-alone consumers and so on. It cannot be ruled out that development of power-intensive heat-accumulating systems using direct chemical transformation methods will result in considerable progress in heat and energy supply.

In order to select energetically and economically advantageous HAM, one has to know their thermal characteristics. Since an experimental study on the complex of properties that is required for estimating the heat-accumulating ability of a melt is commonly a complex task (in particular, reference equipment operated by skilled personnel and long measurements are necessary), it is very important to have methods for the prediction of the heat-accumulating properties of melts based on incomplete or indirect data.

An important place in obtaining the required information on the properties of HAM belongs to approximate calculation methods and prediction with the use of the system approach for discovering the relationship between the thermal properties (reaction heats) and the nature of the components.

The most efficient methods of HAM research are the calculation-experimental ones which combine theoretical calculations with experimental studies. In particular, the HAM properties can be determined with the use of the experimentally studied phase diagrams of multi-component systems. It is this methodological approach that is implied by algorithm considered above (see Scheme 1).

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Sorption-spectroscopic and test methods for the determination of metal ions on the solid-phase of ion-exchange materials

S B Savvin, V P Dedkova, O P Shvoeva

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Abstract. Data on sorption-spectroscopic and test methods for the determination of metal ions on the solid-phase of ion-exchange materials published over the past decade are reviewed. The advantages and disadvantages of ion-exchange materials are discussed. The detection limits and selectivity of these techniques are described. The bibliography includes 151 references.

I. Introduction

In recent years, well-known organic reagents have been employed in sorption-spectroscopic and test methods more extensively than in conventional photometry. These techniques, with the use of the same reagent, allow simultaneous gain in sensitivity and selectivity and considerable reduction of the assay time. Remarkable progress in the analytical chemistry of organic reagents has become possible, in particular, owing to the advent of a new generation of instruments for measuring absorption and reflection of solid materials and organic reagents and complexes immobilised on these solids, *i.e.*, the analytical forms of the elements subject to determination, and of compact mini-pumps with controllable flow rates and novel materials as carriers. All these factors have stimulated the development of a great variety of sorption-spectroscopic techniques for the determination of inorganic compounds using organic reagents.

Various materials, *e.g.*, paper, foamed polyurethanes, silica, cellulose, poly(vinyl chloride) and caprone membranes, fabrics, ion-exchange resins, *etc.*, are used as a solid phase in sorption spectroscopy. This review considers the published data on the use of ion-exchange materials as a solid phase.

II. Sorption-spectroscopic methods

Ion-exchange materials have long been in use as sorbents for the concentration and separation of elements.^{1–4} The history of selective sorption of metal ions on natural and synthetic materials has been described in a monograph.¹

Strongly acidic and strongly basic ion exchangers possess low selectivities. The main procedure for the enhancement of the selectivity of ion exchange materials is the introduction of complexing groups. Complexing sorbents can be synthesised by introducing covalently bound functional groups into the polymer^{1–4} or by modification of ion-exchange and non-ionic resins with organic reagents based on ion exchange or adsorption.^{5,6}

The sorbents with pendent chelating groups are well-known and have found wide application, though they have a number of drawbacks, such as difficulties of their synthesis, low reversibility of sorption–desorption processes, unsatisfactory kinetic characteristics, *etc.* On the other hand, these sorbents are efficient for the concentration and separation of elements with subsequent spectroscopic determination.

Modified ion-exchange resins prepared from conventional ion-exchange resins by sorption of organic reagents have found extensive use in recent years. Some characteristics of complexing sorbents for the concentration and separation of metal ions have been reviewed.⁵ This review considers various types of ion-exchange resins and modifying reagents, their ligand capacity, methods for the determination of metal ions and areas of application of complexing sorbents. It was shown that the retention of a modifying reagent on an ion-exchange resin depends on the type of the modifying reagent, pH of the aqueous solution of the reagent, the nature of the ion-exchange resin and of the exchangeable anion, the structure of resin grains and the stability of the sorbent in different media. The conditions for desorption of the modifying reagent are also described. Other parameters determining the retention and selectivity of metal ion separation on complexing sorbents include the stability of metal complexes with organic ligands and pH of the test solution; the mechanism of the metal ion sorption on a complexing sorbent is similar to that of complexation in aqueous media.

The methods used for the preparation of modified ion-exchangers, their properties and applications are described in a review.⁶ Such ion-exchangers are generally used for the selective and group concentration of elements, but their most valuable property is that they allow simultaneous concentration and determination of the corresponding elements. This has been employed in the most advanced directions of analytical chemistry, *viz.*, sorption-spectroscopic and test methods.

In the choice of optimum conditions for sorption-spectroscopic methods, one should take into account the fact that the behaviour of a complex compound in solution and on a solid phase may be different. The sensitivity and selectivity of the determination depend on the composition of the complex formed, on conditions of sorption and analysis, on the mode of immobi-

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lisation of the reagent on the carrier, on kinetic features of the process and on many other factors.^{7–10}

Depending on the method used to detect the analytical signal, sorption-spectroscopic methods for the determination of elements with the use of modified ion-exchange resins (solid-phase spectrometry) are subdivided into sorption-luminescent, sorption-photometric and diffuse reflectance spectroscopy.

Sorption-luminescent methods are based on the measurement of parameters of the generation or quenching of luminescence in reactions occurring on a solid phase. These methods are not considered in this review.

Sorption-photometric methods (solid-phase photometry) entail the measurement of optical densities of concentrated substances in cells relative to a swollen standard ion-exchange resin having the same degree of granulation, in cuvettes, on neutral glasses or perforated discs, *etc.*, after a complex of the compound to be determined with the reagent has been formed on a solid phase. The methods based on the concentration of the ion to be determined either as such or as its complex on an original or a reagent-modified matrix with subsequent desorption of the complex compound and measurement of the optical density of the eluate, also refer to sorption-photometric methods.

Diffuse reflectance spectroscopy consists in the measurement of changes in the diffuse reflection of the solid phase containing a complex compound relative to an original or a reagent-modified solid phase. The latter two groups of sorption-spectroscopic techniques are closely interrelated and employ virtually identical terminology. The term 'sorption-photometric methods' is often applied to describe the methods involving measurement of the magnitude of diffuse reflection rather than optical density.

The absorption spectra of complexes in solution and the spectra recorded on a solid phase by using sorption-photometric methods are usually similar, which considerably simplifies comparison of their behaviour. The prospects for solid-phase spectrophotometry are considered in a review⁹ which describes its main advantages, such as the possibility of simultaneous concentration and preparation of analytical forms of concentrated substances which are best suited for further analysis, enhanced stabilities of compounds in the sorbent phase in comparison with those in solutions, increased selectivity of action of chromogenic reagents due to greater rigidity of the molecule fixed on a polymeric matrix. Other advantages include the possibility of using both water-insoluble organic reagents immobilised on ion-exchange resins and reactions yielding poorly soluble compounds or colloidal systems, fast reaction kinetics, high degree of extraction and high variability of the solution volume to the adsorbent mass ratio. The reproducibility of experimental results depends on the procedures used for measurement of the analytical signal and sampling.

1. Solid-phase photometry

Solid-phase photometry (ion-exchange photometry or ion-exchange resin absorptiometry) was originally proposed for detecting trace quantities of elements.^{11, 12} The ions to be determined can be immobilised on a solid phase in three different ways, *viz.*, (i) by sorption of the final complex, (ii) by sorption on an untreated ion-exchange resin followed by the formation of a complex on a solid phase and (iii) by sorption on an ion-exchange resin pretreated with a reagent. A design of a photometric cell suitable for a transparent ion-exchange resin for measuring optical density at appropriate wavelengths has been proposed. This method is characterised by high sensitivity and permits for measurement of microquantities of ions in complex mixtures. Thus the sensitivity of solid-phase photometry in the determination of bismuth exceeds that of conventional spectrophotometric procedures 320-fold. Solid-phase photometry was recommended for use in the analysis of natural waters without preliminary concentration of the elements to be determined.^{11, 12}

By virtue of higher sensitivity and selectivity which may be achieved by proper choice of a solid phase and a reagent, solid-

phase photometry is advantageous over spectrophotometry in the determination of nitrite, fluoride and phosphate ions as well as of metal ions, such as zirconium, titanium, copper and uranium.¹³

In the analysis of geological materials, niobium is adsorbed as a complex with sulfochlorophenol C on the anion-exchange resin AB-17,¹⁴ uranium(VI) is adsorbed on AB-17 modified with 2-(2-thiazolylazo)-5-diethylaminophenol.¹⁵ The detection limit for uranium and niobium oxide is $0.1 \mu\text{g ml}^{-1}$. Fe(II), Cu(II), Ni(II), Co(II) and Ti(IV) ions interfere with the determination of uranium. This method is time-consuming, since the sorption and masking of the interfering components take 30 min each.¹⁵

Vanadium(IV) and vanadium(V) are determined using Eriochrome cyanine R immobilised on an anion-exchanger Sephadex DEAE-25. Vanadium(IV) is sorbed first and then vanadium(V) following its reduction with ascorbic acid. Light absorption of the solid phase is measured at 563 and 585 nm in a 1-mm cell; the detection limits of four- and five-valent vanadium is 1.6 and 1.4 ng ml^{-1} , respectively. This method is used for the analysis of natural waters.¹⁶ Modification of the anion-exchanger Sephadex QAEA-2 with 5-bromosalicylhydroxamic acid resulted in a sorbent in which vanadium(V) forms a complex with an absorption maximum at 560 nm. A procedure has been developed for the determination of vanadium(V) with detection limits of 2.2, 1.3 and $0.5 \mu\text{g litre}^{-1}$ in samples with volumes of 100, 250 and 1000 ml and with shaking time 20, 30 and 50 min, respectively. This method was used for monitoring crude oil and drinking water for vanadium.¹⁷

The use of the first derivative of the absorption spectrum in solid-phase determinations increases the sensitivity of the method and diminishes the background effect. The detection limit in the determination of molybdenum with pyrocatechol violet on a solid phase in the analysis of water, soil and plant tissues is from 2 to 8 ng ml^{-1} . The complex (1 : 1) is adsorbed on an anion-exchanger of the dextran type. A cell with an optical path of 1 mm is used and absorption is monitored at 716 nm.¹⁸

Phenylfluorone is used as a complexing reagent for the determination of molybdenum(VI) in sea water; the first derivative of the absorption spectrum of the complex on a nitrocellulose membrane filter is recorded at 536 nm. The concentration of molybdenum in sea water near the Japanese coast was found to be equal to $10.8 \pm 0.4 \mu\text{g ml}^{-1}$ (see Ref. 19).

The method of the first derivative in solid phase spectrophotometry was used for the determination of zirconium on the anion-exchange resin AB-17 modified with Eriochrome Black T,²⁰ and for the determination of lead as an iodide complex on the cation-exchange resin KU-2 modified with Basic Blue K.^{21, 22} The detection limits for zirconium and lead are 0.01 and $0.09 \mu\text{g ml}^{-1}$, respectively.

Flow-injection analysis makes use of reagents immobilised on a solid phase. For example, in the determination of vanadium(V) in natural water, vanadium is first separated from accompanying components by column chromatography on Sephadex G-25, and then is made to react with 2-[2-(3,5-dibromopyridyl)azo]-5-dimethylaminobenzoic acid immobilised on the anion-exchange resin AG 1X2 in a flow of a formate buffer. The optical density of the complex formed is measured at 650 nm. The calibration curve is linear within the range of vanadium(V) concentrations from 2 to $10 \mu\text{g litre}^{-1}$; the productivity of analysis is 5 to 6 samples per hour.²³

Flow-injection systems can be used to determine nickel and zinc by solid-phase spectrophotometry owing to different sorption rates. Nickel and zinc complexes with 1-(2-thiazolylazo)-2-naphthol are adsorbed on silica gel C₁₈. Both complexes are adsorbed at a flow rate of 0.6 ml min^{-1} , but only the zinc complex is adsorbed at a flow rate of 1.5 ml min^{-1} . Analysis can be carried out at zinc and nickel concentrations from 0.1 to 2 mg litre^{-1} . The productivity of the method is 20 samples per hour. The procedure for the determination of zinc and nickel with the help of a flow-injection system was used in the analysis of copper alloys.²⁴

2. Diffuse reflectance spectroscopy

It can be noted that there are much fewer studies in which changes in optical density are measured as an analytical signal than studies making use of diffuse reflection coefficients.

The advantages of immobilisation of analytical reagents on the surface of carriers over photometry of solutions were discussed in a review.¹⁰ It was shown that the combination of sorption concentration with measurements of surface analytical signals makes it possible to reduce the detection limit of components that are detected by several orders of magnitude, while the use of adsorbents modified with specific organic reagents increases the selectivity of analysis. The same paper provides a classification of modified sorbents according to the type of the carrier and the modifying reagent and describes various procedures for the immobilisation of analytical reagents as well as different applications of the modified sorbents for analytical purposes. In particular, immobilisation of organic reagents from polar and non-polar solvents and their mixtures on different carriers under both static and dynamic conditions and after treatment of sorbents with high-frequency low-temperature plasma in the presence of the vapour of organic compounds is considered. Modification of sorbents with inorganic reagents is achieved by sorption or precipitation of metal hydroxides, oxides or salts on the surface. Composite materials based on modified sorbents are obtained in the casting of polyacrylonitrile fibres by filling them with finely dispersed sorbents.

The problem of what is to be called modified organic reagents, modified sorbents and immobilised reagents was raised in a study²⁵ where the terms 'modification' and 'immobilisation' referred to the analytical reagent rather than to the carrier. In their attempt to provide a more exact definition, the authors suggested that organic reagents were considered as modified if a second (or third) modifying (monomeric or polymeric) component reacts with an organic reagent and changes its properties, but no new chemical compound is formed. Upon immobilisation on a solid matrix, the reagent is modified with a polymeric ion-exchange resin. However, the majority of investigators use the following terminology: a reagent is immobilised on a carrier (solid phase), while the carrier (solid phase) is modified with the organic reagent.

The methodology of quantitative measurements in diffuse reflectance spectroscopy is described in the review.²⁶ This study deals with a description of the main factors which affect the accuracy and reproducibility of results of sorption-spectroscopic determination, *viz.*, the particle size, moisture content and magnitude of the mirror reflection superimposed on the diffuse reflection resulting in the distortion of the spectrum. An attempt to relate the analytical characteristics of reactions occurring in solution to those occurring on a solid phase were undertaken in order to predict the possibility of conducting photometric reactions on a solid phase. However, the sensitivity of the sorption-photometric procedure from the optical characteristics of the reagent and the product of the photometric reaction in solution cannot be established *a priori*. Nevertheless, the authors presume that the known values of molar absorption coefficients of complex compounds in solution and the known sensitivity of the sorption-photometric method can be used to predict, with a lesser than 20% error the values of the diffuse reflection coefficients for other compounds with known molar absorption coefficients for the same matrix.²⁶

A study of formation of mixed-ligand complexes of Zn(II), Cd(II), Pb(II) and Ag(I) on silica modified with thiourea derivatives revealed that the rate of formation of such surface complexes depends on the ratio of stability constants of metal–ligand complexes in solutions.²⁷

Modified silica is used for the determination of osmium(VIII) and palladium(II) in wet dedusting sludge and washing acids^{28,29} and for the determination of gold.³⁰ Gold is determined as the metal after thermal treatment of the sorbent and osmium is determined as the oxide. Analytical potentials of silica and foamed

polyurethanes containing *N*-propyl-*N'*-[1-(benzothiazolyl-2-thio)-2,2,2-trichloroethyl]ureido or 4-adamantyl-2-(2-hydroxy-1-naphthylazo)thiazolyl (AOT) groups were examined for possible determination of Pt(IV), Pd(II), Au(III), Ag(I), Cd(II) and Hg(II). It was shown that Hg(II) (pH 6.0–8.5) and Cd(II) (pH 9.5–11.0) are quantitatively retained on the AOT-containing sorbent.³¹

It was demonstrated³² that many regularities of formation of metal ion complexes with organic ligands on the surface of silica gel and in solution are identical for Fe(III), Cu(II), Co(II), Y(III) and La(III). In the case of easily hydrolysable ions, such as Zr(IV), Ti(IV), V(V), W(VI), Mo(VI) and kinetically inert platinum-group complexes, the irregularities are manifested in increased rates of complexation, enhanced complexing ability and formation of mixed-ligand complexes.

The sorption of dithizone (DT), 4,4'-bis(dimethylamino)thio-benzophenone, 4-(thiazol-2-ylazo)naphthol (TAN), 1,10-phenanthroline and high-molecular-weight quaternary ammonium salts (QAS) on silica gel (SG) and cellulose (C) was studied aimed at preparing solid-phase reagents for Hg(II), Ag(I), Pb(II), Zn(II) and Fe(III).^{33–35} It was shown that such sorbents are stable in aqueous solutions in a broad range of pH. The optimum conditions for the formation of Cu(II), Co(II) and Zn(II) complexes with TAN–SG, of Ag(I), Hg(II) and Pb(II) complexes with DT–SG, of Co(II) and Fe(III) thiocyanate and Bi(III) tetraiodide complexes with QAS–SG and QAS–C were established. To this end, a variety of sorption-spectroscopic and test methods as well as reactive indicator papers have been devised for express control of these metal ions in natural, drinking and waste waters and biological fluids. The detection limit for these metal ions lies in the range of 0.2 to 10 µg litre⁻¹ at a sample volume of 50–100 ml.

Optimum conditions for the sorption of Cd(II), Hg(II) and Pb(II) ions on Silochrom modified with 4-(thiazol-2-ylazo)resorcinol were found. These ions were sorbed from an acetate buffer pH 6.8–7.5 (15 ml) on the sorbent (0.3 g) upon shaking for 5–10 min. The concentration coefficient for Cd(II) and Pb(II) was 85, that for Hg(II) was 300. This procedure was used for the analysis of soils.³⁶

The cobalt complex with 1-(2-pyridylazo)-2-naphthol (PAN) is adsorbed on an unmodified silica gel and is firmly retained on the sorbent after acidification with up to 0.5 M HCl. This procedure allows selective determination of 2 to 10 µg of cobalt in drinking and mineral waters. Ballast components are desorbed upon subsequent acidification. The sorption is performed from 100- and 300-ml sample volumes under static conditions; the mass of the silica gel is 0.2 g.³⁷

1-(2-Pyridylazo)-2-naphthol immobilised on Silochrom C-120 is used for the determination of indium. The concentration coefficient for indium adsorbed from a 150-ml sample is 500.^{38,39}

Immobilisation of aluminone on silica gels containing different groups, with different particle diameters and pore sizes was studied as a sensitive layer of an optical sensor for copper.⁴⁰ Immobilisation produced a favourable effect manifested as a longwave shift of the absorption maximum, a decrease in pH for the complexation and an increase in sensitivity and selectivity. A procedure for the detection of copper in foodstuffs with a detection limit of 0.015 µg ml⁻¹ was developed.

Diffuse reflectance spectroscopy was used to study the completeness of sorption of Fe(II) and Fe(III) ions as complexes with catechol-3,5-disulfonic acid on the anion-exchange resin AB-17.⁴¹ This study demonstrated the possibility of separate determination of Fe(II) and Fe(III) ions; a test method was proposed for the determination of iron with a detection limit of 0.01 mg litre⁻¹. Fe(III) ions are determined at pH 3.5, while a sum of Fe(II) and Fe(III) ions, at pH 6–9. The measurements are performed at two wavelengths (500 and 540 nm); the concentrations of Fe ions are calculated from the following equations:

$$\text{Fe(III): } F_{500} = (5.7 \pm 0.05)c + (0.83 \pm 0.04),$$

$$F_{540} = (4.56 \pm 0.05)c + (0.66 \pm 0.04),$$

$$\text{Fe(II): } F_{500} = (4.59 \pm 0.28)c + (0.77 \pm 0.33),$$

$$F_{540} = (3.7 \pm 0.06)c + (0.04 \pm 0.03),$$

where F is the Gourevich–Kubelka–Munk function and c is the iron concentration ($\mu\text{g ml}^{-1}$). Iron ions are determined at concentrations from 0.03 to 6.4 $\mu\text{g ml}^{-1}$.

Colorimetric characteristics of coloured sorbates, *viz.*, luminosity (L), colour coordinates (A , B), saturation (S), brightness (Y), colour tone (T), shading (E), *etc.*, can be used for detecting analytical signals in diffuse reflectance spectroscopy in addition to the diffuse reflection coefficient (R) or the Gourevich–Kubelka–Munk function (F). The use of these colour characteristics as analytical signals makes it possible to determine dissociation constants of organic reagents and increases the sensitivity and accuracy of metal ion determinations. The use of ΔL and ΔY instead of ΔF (where Δ is the difference between the values of the corresponding coefficients for the complex and the reagent) decreases 4- to 20-fold the detection limit for cobalt, indium and nickel with immobilised reagents. According to sensitivity of determination, these values can be arranged in the following order: $\Delta F < \Delta A < \Delta S < \Delta L < \Delta Y$.^{42–49}

The Gourevich–Kubelka–Munk function, which allows the establishment of a correlation between analytical signals in the same photometric reaction occurring both in a solution and on a solid phase, is the most frequently used as the analytical signal. The simplest way to express the analytical signal is to present it as a difference in diffuse reflection coefficients of carriers after the passage of control and test solutions at the optimum wavelength.

The intensities of analytical signals depend on the efficiency of sorption of metal ions from solutions and the completeness of conversion of sorbed metals into coloured complex compounds on a solid-phase. The signals, in turn, depend on the acidity of test solutions (Fig. 1a), the mass of sorbent discs (Fig. 1b) and the composition of the reagent solution.

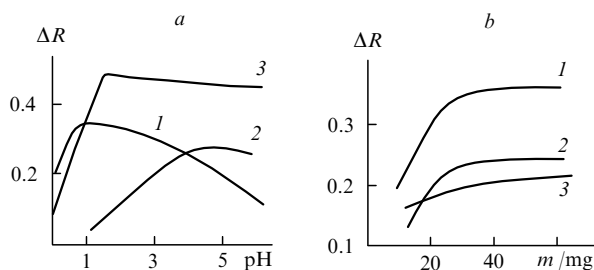


Figure 1. Dependence of the analytical signal of metal complexes on the solid phase of a fibrous sorbent filled with the cation-exchange resin KU-2 on the acidities of solutions (a) and the mass of the sorbent disc (b) in the determination of iron (1), nickel (2) and copper (3) with potassium thiocyanate, dimethylglyoxime and sodium diethyldithiocarbamate, respectively; (a): $c_M = 0.05$ (Fe), 0.1 (Ni), 0.1 mg litre⁻¹ (Cu); (b): $c_M = 0.05$ mg litre⁻¹.

3. Chemical optical sensors

Sorption-spectroscopic methods and immobilised organic reagents were used in the design of the so-called chemical optical sensors or sensitive elements.^{50–85} There are several different interpretations of the term ‘sensor’. Thus a chemical sensor is defined as a probe which provides direct information about the chemical composition of the environment. It consists of a physical transducer of analytical signals and a chemically selective layer.⁵² Chemical sensors are the main elements of a new generation of analytical devices, such as sensor analysers, which, together with a sensitive element, comprise sample injectors and various devices for the processing of signals and displaying the results, *viz.*, the

concentration of the tested substance.^{53,54} In other studies,^{55,56} a sensor is referred to as a primary device which selectively responds to changes in definite properties of the environment by converting this information into the corresponding electrical signals, *e.g.*, optical signals. We define a sensor as a sensitive element of a sensor analyser.

Sensors are supposed to be recoverable systems, *i.e.*, they must easily be reset after the assay is completed. Therefore, the material used as a solid phase should first of all be mechanically and chemically stable. Fibrous materials filled with ion-exchange resins largely meet these requirements.

These materials are cast from suspensions of finely dispersed ion-exchange resins in a solution of polyacrylonitrile in dimethylformamide. Pressing of suspensions through spinnerets produces thin porous polyacrylonitrile fibres filled with ion-exchanger particles. The diameter of a polyacrylonitrile fibre is 30 to 40 μm , the size of carrier particles is 5 to 10 μm , the degree of filling is 50 mass %–75 mass %. By virtue of their fibrous structure and high degree of dispersion of filling agents, such materials manifest remarkable kinetic properties.

Carriers represent white or light-yellow 0.1–0.2 mm thick fibrous plates having a density of 40 to 80 g m^{-2} which are stable in strongly acidic, neutral and weakly alkaline media. These plates are used to manufacture discs. Depending on their diameter, 10 or 20 mm, thickness and degree of filling, the mass of discs varies from 10 to 50 mg.

Prior to use, carriers (in the form of plates or prefabricated discs) are washed with 2 M HCl up to a negative reaction for Fe(III) with thiocyanate ions and then with water up to a negative reaction for chloride ions with silver nitrate and dried in air. Such carriers can be stored at room temperature for an indefinitely long period of time. Prior to use, plates are shaped into discs and swollen in water for at least 24 hours.

Immobilisation of analytical reagents is performed in a static or a dynamic regime. In the former case, the discs are kept in aqueous or aqueous–organic solutions of reagents (10^{-5} – 10^{-6} M) for 5–15 min and then washed with water. The concentration of the immobilised reagent varies from 10^{-6} to 10^{-4} mol litre⁻¹ g⁻¹. In the latter case, the reagent solution is dripped or pumped through the carrier disc placed in a cell with a sintered-glass filter using a peristaltic pump.

Filled fibrous sorbents can be used in both modified (*i.e.*, after immobilisation of the organic reagent) and in the original (colourless) form.

Ions to be determined are concentrated in different ways, *viz.*, directly from the test solution with subsequent detection on a solid phase, by concentration of a complex compound formed in the solution and by sorption of the ion in question on a carrier with an immobilised reagent.

Apparently, sorption of a preformed complex is the least appropriate solution of the problem of increasing the sensitivity and selectivity of the method. The advantages of discs with immobilised reagents are as follows: full readiness of the so-called sensitive element for the assay, simplicity and lack of necessity to prepare reagent solutions. Of their disadvantages one may relate limited durability and storage life; nor in all cases can they be recovered.

The obvious merits of colourless discs are that they are easily recovered and that the same discs can be used for the determination of different elements. Another advantage is that the storage life of carriers is not limited. Their demerits are as follows: the necessity to prepare reagent solutions and the need for an additional procedure, the so-called ‘development’, *viz.*, sorption of a reagent on a carrier after concentration of the ion in question.

On the whole, the main attraction of fibres filled with ion-exchange resins is the possibility to vary the degree of their filling and the nature of the ion exchanger and the reagent depending on a concrete selectivity problem. In contrast with other carriers, these materials represent both the sites for colour reactions and the means for concentration of ions to be tested and removal of

ballast components. They are resistant to mechanical actions and manifest high sorptive and kinetic properties, which ensures a high level of sensitivity, which can be attained by passing any volume of test solutions. The use of fibrous materials ensures easy sorption of reagents and tested ions (*e.g.*, by immersion of the carrier into the solution or by passing the solution through the carrier) and easy separation of the solid phase from the solution (*e.g.*, by decanting under static conditions or by pumping under dynamic conditions). This, in turn, allows easy automation of flow sorption-spectroscopic procedures and, if necessary, test operation without any devices based on visual detection.

Studies of fibres filled with ion-exchange resins used as sorbents follow two main lines which include sorption-spectroscopic determination of metal ions based on changes in their diffuse reflection upon complexation with organic reagents on a solid phase (carrier) and elaboration of test methods.

These studies were undertaken with the view of constructing recoverable systems which utilise exclusively fibrous sorbents with immobilised reagents as optical sensors. However, despite its indisputable advantages, this approach significantly restricts the potentials of a new carrier. It was found that organic reagents immobilised on carriers are not always effective in analytical reactions or they change their colour upon immobilisation. Regeneration of optical sensors with immobilised reagents is a complicated task. On repeated regeneration, organic reagents are either destroyed or washed off from the carrier with a regenerating solution. Nevertheless, in some cases sensitive elements can be recovered. Thus in the determination of lead with Xylenol Orange⁵¹ and in the determination of uranium with Arsenazo I,⁶⁴ the same sensitive element (the optical sensor) can be used for up to 20 assays. Most frequently, optical sensors cannot be regenerated at all, *e.g.*, a sensitive element for thorium with Xylenol Orange.⁵¹ It is economically more advantageous to replace a sensitive element used as a chemical optical sensor than to regenerate it.

Two types of sensitive elements or chemical optical sensors are presently being developed, *viz.*, fibrous materials filled with ion-exchange resins with and without organic reagents immobilised on them. In the latter case, the analytical reaction with an organic reagent is accomplished after sorption of the tested ion.

In the choice of a particular organic reagent, preference should be given to the most well-studied and accessible reagents possessing good analytical characteristics. Organic reagents containing acid groups are immobilised on materials filled with anion-exchange resins; while those containing basic groups are sorbed on cation-exchange resins. In a few studies, sorption was performed on ion-exchange fabrics with phosphate or vinylpyridinium groups.

Fixation of reagents on solid carriers occurs mainly due to the ion exchange mechanism and partially due to adsorption, formation of hydrogen bonds and other interactions.

Electron and EPR spectroscopy was used to study the properties of 1-(2-pyridylazo)-2-naphthol (PAN) immobilised on polyacrylonitrile fibres filled with finely dispersed ion-exchange resins and its complexes with copper(II).⁶⁶ In this study, fibres filled with different ion-exchange resins, *viz.*, KU-2, KB-4, AB-17 and A-5, were employed. The parameters of EPR spectra of copper complexes on a solid phase in the pH range of 1–8 were calculated. It was shown that immobilisation of PAN on a solid phase changes its state (*viz.*, the spread of individual ionic forms of the reagent is shifted and widened) and spectroscopic properties. If the concentration of the reagent exceeds 10^{-5} mol litre⁻¹ g⁻¹, this undergoes association on the surface of the carrier. The main contribution to the retention of PAN on these ion-exchange resins is due to ionogenic groups of the carrier; however, under certain conditions, adsorption begins to play a leading role, as is the case with the adsorption of PAN on KU-2 in alkaline media.

The role of the nature of the carrier in complexation is rather complicated and ambiguous and is manifested primarily in its competing interaction with metal ions. By using different carriers,

one can vary the concentration of the immobilised reagent on the surface and thus control its reactivity.

The second type of chemical optical sensors proved to be more advantageous than first type sensors. Their additional advantages are as follows. Since sorption and determination are separated by certain time interval, it is possible to introduce masking complexing agents in the concentration and determination steps, which considerably increases the selectivity of the reactions. Also, this particular type of sensor makes use of the original, colourless carriers. This circumstance has stimulated the development of new spectroscopic solid-phase methods (*e.g.*, determination of cations on a solid phase), which consists, for example, in the sorption of metal cations in the form of colourless or weakly coloured anionic complexes on anion-exchange resins and their subsequent detection in the most contrasting colour reaction. Thus the sensitivity of determination of Fe(III) with thiocyanate on the anion-exchange resin AB-17 increases considerably if iron is sorbed in the form of complexes with tartaric or glycolic acids (Fig. 2).^{67,68} Comparative data on iron determination with thiocyanate following sorption from solutions of glycolic acid on KU-2- or AB-17-containing fibres testify to a significant increase in selectivity. The selectivity factors are equal to 10 and 20 for Zn, 20 and 50 for Cd, 5 and 200 for the uranyl ion, $\ll 1$ and 10 for Bi and 100 and 3000 for oxalates and phosphates, respectively.

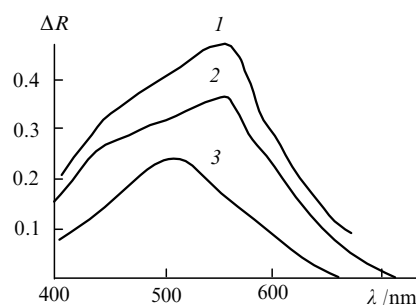


Figure 2. Reflection spectra of the iron thiocyanate complex formed upon sorption of Fe(III) from 0.01 M solutions of glycolic (1) and tartaric (2) acids and without addition of anions (3) on a fibrous material filled with the anion-exchange resin AB-17; $c_{\text{Fe}} = 0.2 \mu\text{g ml}^{-1}$.

The new methodology has made possible solid-phase determination of thorium with Arsenazo III. The latter is the best reagent for thorium; however, it changed its colour upon sorption on a carrier, which prevented the assay. If thorium in the form of the oxalate complex is sorbed on fibres containing an anion-exchange resin, it can be determined in the form of the complex with Arsenazo III on a solid phase in strongly acidic media. In this approach, the detection limit is 0.2 ng ml^{-1} (the sensitivity of photometric determination of thorium with Arsenazo III is $0.01 \mu\text{g ml}^{-1}$). Uranium, zirconium, titanium, lanthanum, iron, fluorides and phosphates do not interfere with the determination.^{69,70}

Fibrous adsorbents filled with ion-exchange resins (AB-17, A-5, KU-2) and the styrene–divinylbenzene copolymer containing no ionogenic groups were studied as possible carriers for a sensitive element for mercury with 4-phenylazo-3-aminorhodanine.⁷⁹ It was found that the reagent is tightly bound only to carriers containing ionogenic (both cationic and anionic) ion-exchange groups. However, the sensitive reaction of mercury with the immobilised reagent occurred only on fibres with the cation-exchange resin KU-2. A method has been developed for detecting mercury in waters with the detection limit of $0.02 \mu\text{g ml}^{-1}$.

Sensitive optical elements for uranium, mercury and lead have been proposed, which are based on the formation of complexes with Arsenazo III, dithizone and hexaoxacycloazochrome, respectively.⁸⁰ In these studies, polyamide, poly(ethylene terephthalate) and cellulose membranes were used as carriers.

These membranes are made of transparent or semi-transparent materials and are resistant to dilute alkalis and acids. Immobilisation of reagents is carried out in a static or a dynamic mode. In the dynamic mode, the solution is allowed to pass over the membrane surface if the pore diameter is less than 0.45 μm . In the case of larger pores, the solution is filtered through the membrane. The ranges of direct determination in water are 0.01 to 0.10 for uranium, 0.005 to 0.05 for mercury and 0.05 to 0.5 mg litre^{-1} for lead.

The possibility of selective determination of uranium(VI) at the level of $2 \times 10^{-8} \text{ mol litre}^{-1}$ in the presence of a 100-fold excess of thorium by diffuse reflectance spectroscopy has been demonstrated.^{81, 82} In these studies, polycapromamide and nylon

membrane filters were used as matrices. The diffuse reflection coefficient, R , is fixed at 660 nm for uranium and 680 nm for thorium and the uranium concentration is determined from a system of equations:

$$R = \varepsilon_U c_U l + \varepsilon_{Th} c_{Th} l,$$

$$c = c_U + c_{Th},$$

where R is the diffuse reflection coefficient, ε is the molar adsorption coefficient, c is the concentration (mol litre^{-1}) and l is the membrane thickness.

The conditions of sorption of azorhodanines, tyrodine and sulfonitrophenol M on polymeric carriers, e.g., caprone mem-

Table 1. Some characteristics of sorption-spectroscopic methods for the determination of metal ions using fibrous materials filled with ion-exchange resins.

Ion (I)	Fibre (fabric)	Sorption conditions	Reagent	Detection limit /mg litre ⁻¹	Selectivity factor		Ref.
					M	[M/I]	
Cu(II)	KU-2	pH 1, C ₆ H ₈ O ₆	PAN	0.03	Zn, Cd, Hg, Pb, V, Al, Mn, Ni	> 1	72
	KU-2	0.04 M HNO ₃	DETC + EDTA (pH 8.5)	0.002	Zn, Cd, U Fe(III), Ni Co	100 50 10	76
Fe(III)	KU-2	0.1 M HNO ₃	KSCN	0.01	Ni	200	76
					Co	50	
					Cd	20	
					Zn	10	
					U(VI)	5	
					Cu	2	
Ni(II)	KU-2	pH 4.5	DMG, 2% NH ₃	0.005	d, Zn	100	76
					Bi	10	
Ag(I)	KU-2	pH 3	Rhodazole X	0.005	Fe(III), Cu, Co	5	85
					Fe, Ni, Co, Zn, Pb,		
					Pd, Ca, Mg	100	
					Cu	10	
					Hg	2	
Hg(II)	KU-2	pH 1	PAAP	0.02	Pb, Cr, d, Ni, Co, Zn	> 10 ³	79
					Fe, Cl ⁻	> 10 ²	
					Cu	50	
Pd(II)	KU-2	0.01 M HNO ₃	NDEA, pH 2–3	0.0005	Au, Pt, Ru	100	77
					Rh, Ir	1000	
Pb(II)	A-5	pH 5	KO	0.004	Al, Ni, Cu, Zn, Sn	4	51
U(VI)	A-5	pH 6	Arsenazo I	0.007	Fe(II)	100	64
					Fe(III), La	20	
					Al, Th	10	
					Zr	1	
V(V)	AB-17	pH 3.5, NaF, H ₂ O ₂	PAR, 0.1 M HCl	0.002	Zn, Mn, Cr(III), Al	> 100	78
					Fe(III), Cr(VI)	50	
					Cu	20	
					Mo	5	
Cr(VI)	AB-17	pH 2	DPC, 0.05 M H ₂ SO ₄	0.0005	Ca, W, Fe(III), Cr(III), Hg	> 10 ³	71, 74, 87
					V, Zn, Co, Ni, Al,	> 10 ²	
					Cu, Mo, Mn, Pb, Cd		
Th(IV)	AH-31	H ₂ C ₂ O ₄ , pH 2	Arsenazo III, 4 M HCl	0.0002	F ⁻ , PO ₄ ³⁻	> 10 ³	70
					Fe(III)	300	
					La, Ti	50	
					Zr	10	
					U(VI)	5	
Zn(II)	F(I)	pH 10, Na ₂ B ₄ O ₇	DT + DETC + + Na ₂ B ₄ O ₇	0.02	Fe(III), Cu, Co, Ni, Pb	> 1	75
Co(II)	F(II)	pH 5	PAN, 0.05 M HCl	0.0005	Fe(III), Mn	100	73
					Cu, Zn	10	
					Ni	5	

Notes. Abbreviations: PAN, 1-(2-pyridylazo)-2-naphthol; DETC, sodium diethyldithiocarbamate; EDTA, ethylenediaminetetraacetic acid; DMG, dimethylglyoxime; PAAP, 4-phenylazo-3-aminorhodanine; NDEA, *p*-nitrosodiethylaniline; XO, Xylenol Orange; PAR, 4-(2-pyridylazo)resorcinol; DPC, 1,5-diphenylcarbazine; DT, dithizone; F(I), fabric with vinylpyridine groups; F(II), fabric containing PO₃H₂ groups.

branes, fibrous materials filled with cation- and anion-exchange resins and fabrics with ionogenic groups, were studied in the development of sensitive elements for Hg(II), Cu(II), Ag(I), Au(III), Pt(IV) and Pd(II). It was shown that azorhodanines and sulfonitrophenol M immobilised on caprone membranes can be successfully used for the determination of these metal ions with the detection limit of 1 to 15 $\mu\text{g litre}^{-1}$.

A procedure has been developed^{83–85} for the determination of silver based on its sorption on discs from polyacrylonitrile fibre filled with the cation-exchange resin KU-2 with subsequent detection with rhodazole X; the detection limit is 5 $\mu\text{g litre}^{-1}$.

The main characteristics of methods for sorption-spectroscopic determination of metal ions which employ fibrous materials filled with ion-exchange resins and fabrics carrying ionogenic groups as solid phases are summarised in Table 1.

III. Instruments

Optical sensors for recording analytical signals are used in mini-devices of the well-known companies 'Specord', 'Spectroton', 'Pulsar' and 'Multitest', in mini-photometers 'Merck', *etc.* Recent publications describe two more devices. One of them was developed at the Institute of Analytic Instrumentation of the Russian Academy of Sciences and represents a small-size chemosensor analyser designed for the determination of pH and concentration of metal ions; its operation is based on the principle of reflective photometry of chemosensors made of optically transparent polymers containing organic reagents.⁸⁶ Its designers sought to build a specialised instrument for implementation of one or several similar analytical procedures with the aid of sensors having a universal configuration. This approach permits one to perform the measurements in three different regimes, *viz.*, measurements of light absorption of the tested object ($-\log R$) relative to the diffusely reflecting substrate or an analogous object with the known characteristics. The second and third regimes are intended for procedures utilising definite types of sensors and allow for calibration. Chemosensors for measuring pH and concentrations of Fe(III), copper and rare-earth metal ions at the level of 2×10^{-3} – 2×10^{-5} mol litre⁻¹ have been developed.

The apparatus (150 $\times$ 130 $\times$ 80 mm) has a weight of 1 kg (the volume of the samples varies from 5 to 70 μl) and can be used for measuring reflective properties of coloured reagent papers and multilayer sensitive elements. The measurements are performed at wavelengths from 530 to 700 nm. The duration of the exposure of the sensitive element to the sample is 90–120 s. The apparatus operates on alternating current or utilises the energy of internal accumulators.

The second instrument, *viz.*, the optical sensor analyser OSA-TM developed at the Scientific-and-Industrial Corporation 'Kvant' (Rostov-on-Don), is intended for environmental monitoring of natural, drinking and purified waste waters for heavy metals at the MPC and lower levels under both laboratory and field conditions.⁸⁷ It is designed as a colorimetric densitometer and is used for measuring diffuse reflection coefficients of optical sensors in flow-through cells as well as for measuring optical densities of coloured solutions in cells for liquid samples. This apparatus (370 $\times$ 220 $\times$ 100 mm) has a weight of 4.5 kg and operates on alternating current or utilises the energy of accumulators. It is supplied with an integral flow-through optical cell, a peristaltic pump, a microprocessor with push-button control and eight light filters operating at 400–750 nm. Its operation is based on the detection of changes in colour (*e.g.*, reflection with optical sensors or the optical density of the tested solution) as a result of interaction of metal ions with analytical reagents. The analytical signals are shown on a digital display as the transmission (reflection) coefficient, optical density and concentration of metal ions in the tested solution.

The potentials of OSA-TM are exemplified⁸⁷ in the determination of chromium(III) and chromium(VI) in surface waters. Chromium(III) is measured photometrically with Arsenazo III,

while the concentration of chromium(VI) is determined in a flow-through cell with anion-exchanger filled fibres using complexation with 1,5-diphenylcarbazine on the solid phase. A method was proposed for the simultaneous determination of chromium(III) and chromium (VI) in sanitary–general-purpose water up to 1 : 5 ratio at the concentration of Cr(III) > 0.2 MPC and that of Cr(VI) > 0.1 MPC. The duration of one assay is 10 to 20 min.

A procedure for sorption-spectroscopic assay utilising optical sensors is simple with this instrument. A carrier disc ($\varnothing$ 10 mm) is placed in a flow-through cell and the test solution is pumped through the disc at a rate of 10 ml min⁻¹ under optimal sorption conditions. If unmodified carriers are used, the reagent solution is pumped through under optimum assay conditions after which the diffuse reflection coefficient is measured.

The main advantage of the OSA-TM analyser is that it allows both routine photometric measurements and measurements in flow-through optical cells where the sorption of the tested ion occurs. The reaction of the ion takes place on a solid phase and is followed by measurement of the analytical signal. A combination of these three processes in a single flow-through cell not only simplifies the procedure but also increases significantly the reproducibility of experimental results owing to the omission of one step, *i.e.*, the transfer of the optical sensor from the sorption cell to the measuring cell, which excludes any fluctuations in the sensor wetness. The use of the instrument allows for rapid presentation of experimental results in units of concentration. The construction of the instrument with a flow-through optical cell became possible due to development of optical sensors in which fibrous materials filled with ion-exchange resins or fabrics containing ionogenic groups are used as carriers.

IV. Test methods

Numerous versions of test methods are being actively developed.^{88–104} The materials used as carriers for sorption-spectroscopic assays, such as reagent papers, foamed polyurethanes, silica gel, membranes, ion-exchange resins, *etc.*, are also employed in test methods. Indicator test systems, *e.g.*, from 'Merck', are currently known.

Some densitometric characteristics for express tests have been obtained which are based on the use of reactive reagent papers⁹⁶ and are designed for the determination of certain elements with the help of reflective electronic mini-photometers equipped with light-emitting diodes operating at wavelengths of 567 $\pm$ 15 and 660 $\pm$ 10 nm and a modified device for concentration of 10⁻⁷ mass %–10⁻⁵ mass % of components in aqueous media.

The main requirements for test reactions are as follows:¹⁰¹ high sensitivity (not lower than MPC); high light-transition contrast; proximity of the optimum acidity of assays to the acidity of the tested solution; stability of external effects for a sufficiently long time and upon exposure to light; the possibility to preserve the test form after positive response for subsequent quantitative assay under laboratory conditions; and selectivity.

The methodological aspects of detection and processing of analytical signals in colorimetry have been reviewed.^{48, 101} The general colour discrimination criterion (ΔE) is the main parameter in making a test scale. In order to increase the sensitivity of a test reaction, special parameters, such as whiteness (W) for colourless sorbents and yellowness (G) for blue-coloured complexes have been introduced. The calibration test scale is built up from the known dependence of the general colour discrimination on the concentration of the tested element. One unit of ΔE corresponds to one colour discrimination threshold; therefore, the concentrations of tested elements are selected in accordance with the corresponding magnitude of ΔE . A reliable sense of difference in light flux intensities is reached if this difference is at least 10%. Therefore, discrete values of colour discrimination with $\Delta E > 10$ are especially preferred in the case of diffuse reflection. If the tested sample loses its colour or is bleached in the course of an

analytical reaction, its whiteness is used for building up a test scale:

$$W = 100 - \Delta E.$$

The lower threshold of tested concentrations in any test method is defined as general colour discrimination (10 arbitrary units) between the original test sample (E_0) and the test sample following its reaction with the tested element (E):

$$E - E_0 = 10 \text{ or } W_0 - W = 10.$$

In the building up of a test scale, one should not go beyond the limits of saturability (ΔS) of the tested sample (20%–60%) which corresponds to the upper threshold of tested concentrations.

The contrast of a colour reaction is enhanced after application of optical bleaching compounds onto the matrix surface; their operation principle is fluorescence. The presence of these compounds does not influence chemical and analytical characteristics of immobilised reagents. In their presence, reagents are rapidly and evenly distributed over the matrix surface and are well retained in acid media under both static and dynamic conditions. For example, the detection limit in the determination of uranium(VI) with Arsenazo III and application of optical bleaching is $0.001 \mu\text{g ml}^{-1}$. The colour of the complex compound is bright green, whereas in the absence of the bleaching agent the complex has a grey-blue colour and has a detection limit of $0.1 \mu\text{g ml}^{-1}$ (see Ref. 102).

A portable field test system for the determination of numerous elements in water, soil and rainfall has been developed.^{103, 104} This assay includes the following steps, *viz.*, measurement of the lengths of coloured or bleached zones on reactive reagent papers cut into stripes and pasted into a polymeric film one end of which is brought into contact with the tested fluid, visualisation of colour intensity, measurement of the area of the coloured or bleached zone and visualisation of colouring of the tested fluid after application of reagent papers. The range of tested concentrations is $0.001 - 1000 \text{ mg litre}^{-1}$.

1. Reagent test papers

The majority of publications devoted to test methods deal with reagent papers.^{88–121} Heavy metals on the whole are determined with the help of a device which is similar to that used for air sampling (the detection limit is up to $10^{-7} \text{ mol litre}^{-1}$) which employs test papers impregnated with potassium tetraborate and PAN.¹⁰⁷ Rapid tests for the determination of toxic elements in water are carried out on papers, films or glasses with the detection limits of 0.05 for Cu(II), 0.2 for Fe(III), 0.5 for Co(II), 0.03 for Mn(II) and $0.03 \text{ mg litre}^{-1}$ for V(V) (see Ref. 108).

Iron ions are determined on reactive test papers with detection limits ranging from 0.02 to $0.2 \text{ mg litre}^{-1}$ depending on the method (see Refs 109–111). A tape method was proposed for the determination of Fe(III) ($0.5 - 3.5 \text{ mg litre}^{-1}$) on papers impregnated with the anion-exchange resin Amberlite IRA 400 modified with sodium ethylenediaminedi(hydroxybenzylphosphonate).¹¹²

Immobilisation of pyrazole-containing formazanes and hydrazones on the base-paper increases their sensitivity with respect to transition metals. Express tests for determining Cu(II), Ni(II) and Co(II) at the level of $10^{-7} \text{ mass \%} - 10^{-8} \text{ mass \%}$ have been developed.¹¹³ Test paper impregnated with Michler's thio-ketone, potassium dihydrogenphosphate, sodium thiosulfate (in order to reduce copper and remove active chlorine) and Triton X-100 was proposed for the determination of copper in drinking water (the detection limit is $0.05 \text{ mg litre}^{-1}$);¹¹⁴ test paper containing the nickel complex with 2-nitroso-1-naphthol, diphenylguanidine, thiourea and ammonium fluoride was used for the determination of cobalt.¹¹⁵

An express test method for the determination of manganese in drinking water is carried out on paper containing a multicomponent reagent. This analysis is based on the measurement of the time interval during which the indicator zone changes its colour as

a result of oxidation of Malachite Green with potassium periodate (KIO_4) catalysed by manganese(II) ions. The detection limit is $0.03 \text{ mg litre}^{-1}$ (see Ref. 116).

Zinc ions are determined in foodstuff using reagent test paper (FMOPF-6C) at pH 8.0. The effect of copper ions is eliminated by addition of thiourea.¹¹⁷ Reagent test paper was recommended for use as indicators for multicomponent assay of water.¹¹⁸

Ion	Concentration range /mg litre ⁻¹	Ion	Concentration range /mg litre ⁻¹
Pb(II)	0.001–0.1	Bi(III)	0.001–0.1
Cu(II)	0.001–0.1	Fe(II)	0.01–0.2
Fe(III)	0.01–0.2	Hg(II)	0.2–2
Cr(VI)	0.1–5		

Lead ions are determined using a reagent test paper (RTP) metal test after its fast separation from Cu, Fe and Zn in aqueous solutions (pH 6.0), emulsions and suspensions using the sensor filter of a pocket indicator ultrafiltration unit.¹¹⁸

Stripes of reagent paper are used for the quality control of water;¹¹⁹ paper stripes impregnated with diphenylthiocarbazone are used for test determination of trace amounts (15 ppb) of lead in drinking water,¹²⁰ while paper stripes soaked with a covalently bound multidentate chromogenic reagent of the formazane type are used for the determination of mercury with a detection limit of $0.05 \text{ mg litre}^{-1}$ (see Ref. 121).

The detection limit in enzymic determinations of mercury and organomercurials on foamed polyurethanes, paper and chitosan with immobilised peroxidase is $10^{-5} \mu\text{g ml}^{-1}$, *i.e.*, below the MPC for mercury.^{122–127} A sorption-catalytic procedure for the determination of manganese¹²⁸ is based on preliminary concentration of manganese(II) ions on cellulose filter paper with chemically bound diethylenetriaminotetraacetate groups (DETATA) and subsequent catalytic oxidation of 3,3',5,5'-tetramethylbenzidine with KIO_4 . The optimum conditions for this reaction in solution and on filter paper were found to be different. Preliminary concentration of manganese on DETATA-paper allows for a nearly 10-fold decrease in the detection limit (up to $6 \times 10^{-6} \text{ mg litre}^{-1}$) and expands the range of tested concentrations up to $5 \times 10^{-6} - 2.5 \times 10^{-3} \text{ mg litre}^{-1}$. The selectivity of the assay is higher in this case: after preliminary concentration from a 20-ml sample, determination of 1 ng of manganese is insensitive to a 1000-fold molar excess of other ions. This method is applied in the analysis of tap and river water.

An express test for the detection and determination of vanadium, which catalyses the oxidation of *p*-diethylaminoaniline with bromate, on glass or poly(methyl methacrylate) at pH 4–5 has been developed. The detection limit decreases in the presence of ferrone which potentiates the catalytic effect of vanadium. This determination is selective with respect to many metals. The interference of Fe(III) ions is eliminated with fluorides. The detection limit for vanadium is $0.09 \text{ mg litre}^{-1}$ (see Ref. 129).

The approaches used in test methods are very diverse. For example, in one of them the analyte is concentrated in a limited area on a hydrophobic surface by evaporation and the element is detected by colour reaction or fluorescence. This procedure is used to determine aluminium with Xylenol Orange in tap water at pH 8.0 or with lumogallione at pH 7.0 (the detection limit is 2.7 ppb) (see Ref. 130).

Molybdenum is determined by an ion-exchange drop reaction with azide with the detection limit of $2 \mu\text{g}$ in 0.09 ml of the sample using the anion-exchange resin Bio-Rad AG 1X8.¹³¹ In the determination of chromium(VI), five to ten beads of the anion-exchange resin Amberlite IR-120 (H-form) are placed onto a white plate and Malachite Green is added (drop reaction). The green colouring of the resin surface observed after 10 min points to the presence of chromium; the detection limit is $1.6 \mu\text{g}$.¹³²

Iron ions are determined on the anion-exchange resin AB-17X8Cl with the detection limit of $0.01 \mu\text{g ml}^{-1}$ (see Ref. 41). Polyester fabric based on poly(ethylene terephthalate)

is used as a substrate for an array of multipurpose indicators. This procedure permits complete elimination of cross contamination of reagent paper stripes with chemical reagents from adjacent stripes.¹³³

2. Silica gel

Test methods on silica gel have attracted attention in the past decade.^{8, 34, 49, 134–140} It was found⁴⁹ that the optical characteristics of Fe(III), Cr(VI), Mn(II), Ni(II), Cu(II) and Zn(II) complexes with PAN on Silochrom C-120 are very similar to those in solution. Thus sorption of 1-(2-pyridylazo)-2-naphthol and 4-(2-pyridylazo)resorcinol (PAR) from aqueous solutions of various acidities was investigated and the conditions for the preparation of modified adsorbents with predetermined capacity with respect to azo compounds were established. Sorption of PAN and PAR on Silochroms C-80 and C-120 was studied under static conditions.¹³⁴ A procedure has been developed for the determination of the reagents in the sorbent phase. The indirect assay consists in the measurement of changes in light absorption of solutions after immobilisation. Alternatively, azo compounds are determined upon oxidation with cerium(IV) in the modified sorbent phase. Maximum modification of the silica surface is observed at pH < 3. The protonated form of PAR is the most intensively adsorbed on silica hydrated to the greatest degree. The completely dissociated form of PAR is not adsorbed by the silica surface. The degree of adsorption of PAN at pH 4.0 decreases as the proportion of acetone in the tested solution increases. At an acetone concentration of 60 vol. %, PAN is not adsorbed on silica surface. Complete adsorption of PAN with Silochrom C-120 usually takes 20 minutes.

It was found that the efficiency of sorption of azo compounds depends on the structure of the silica, its porosity and specific surface. With an increase in specific surface, sorption of the reagent increases. At lower specific surface, the greater part of the reagent diffuses into the sorbent and the pore sizes thus become critical. It was found that adsorbents with a low capacity with respect to the reagent (*e.g.*, < 25 $\mu\text{mol g}^{-1}$) are more preferable for use in test methods (see Ref. 134).

The colorimetric method was used for separate determination of Cu [(0.4–22.0) $\times 10^{-6}$ mass %] and Zn [(3.8–39.0) $\times 10^{-6}$ mass %] in natural water on PAN-modified silica.⁴⁸ Cobalt was determined with PAN immobilised on silica gel¹³⁵ using a test method based on colour discrimination by luminosity (the detection limit is 0.004 $\mu\text{g ml}^{-1}$); its quantitative determination was performed using the Gourevich–Kubelka–Munk function (the detection limit is 0.03 $\mu\text{g ml}^{-1}$). It was found that on going from diffuse reflection coordinates (ΔF) to sorbate colour coordinates (ΔL) with a test reagent, the sensitivity and reproducibility of determination of cobalt increase 4- and 1.5-fold, respectively. 4-(2-Thiazolylazo)resorcinol immobilised on silica gel was recommended¹³⁶ as the test reagent for Co(II), Pd(II) and U(VI) (the detection limits are 0.02, 0.005 and 0.03 $\mu\text{g ml}^{-1}$, respectively).

Test methods for the determination of Co(II), Cu(II) and Zn(II) with 1-(2-thiazolylazo)-2-naphthol, for the determination of Ag(I), Hg(II), Pb(II) with dithizone and for the determination of Co(II), Fe(III) and Bi(III) thiocyanates with quaternary ammonium salts on silica gels and cellulose have been developed.³⁴

The optical and colorimetric characteristics of immobilised 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol and its complexes were obtained in the analysis of sorption of indium and uranium(VI) ions on Silochrom C-120. Test methods for the determination of indium with a detection limit of 0.002 $\mu\text{g ml}^{-1}$ (see Ref. 44) and uranium with a detection limit of 0.25 $\mu\text{g ml}^{-1}$ (see Ref. 137) have been developed; subsequent determination of uranium by diffuse reflectance spectroscopy in the sorbate phase reached a detection limit of 3.5 ng ml^{-1} . The optimum conditions for the formation of uranium(VI) complexes with PAR immobilised on KU-2, foamed polyurethane and Silochrom C-120 were established as pH of 5.8–8.2 and an equilibration time of 20, 20 and 15 min, respectively. An advantage of PAR immobilised on

KU-2 is that it elicits analytical signals of greater magnitude and produces a broader plateau on the optical density versus pH of the complex solution curve. This reaction is selective in the presence of cyclohexanediaminetetraacetic acid; the detection limit is 0.1 $\mu\text{g ml}^{-1}$ (see Ref. 138).

A linear-colouristic method^{141–143} is based on the linear dependence of the length of the coloured zone of the display tube on the concentration of the tested compound. In this procedure, hydrophobic carriers, such as silica gels Diasorb-C₁₆ and Diasorb-phenyl, are modified with known analytical reagents. The dimensions of the coloured zone depend on the nature of the carrier, quantity of the adsorbed reagent, internal diameter of the display tube, flow rate and pH of the sample. By varying tube diameter, one can change the concentration range of the tested element. The detection limits for various elements vary from 10^{-8} to 10^{-6} mol litre⁻¹.

Silica gel modified with lead diethyldithiocarbamate can be used as the indicator powder for the determination of copper ions with a detection limit of 1.5×10^{-8} mol litre⁻¹ in the presence of 1000-fold excess of Ni(II), Zn(II), Cd(II) and Co(II).¹⁴¹ PAN and Xylenol Orange immobilised on silica gel are used for the determination of copper and iron.¹⁴² At equal concentrations of these ions (< 5×10^{-6} mol litre⁻¹), two differently coloured zones are formed in the tube filled with silica gel Diasorb-phenyl-PAN, *viz.*, crimson (Cu) and green (Co).¹⁴² The possibility of determination of cobalt and Fe(III) in the same sample at the MPC level with the use of a tube filled with silica gel Diasorb-C₁₆ modified with 1-nitroso-2-naphthol was demonstrated.¹⁴³ This method is characterised by ease of tube preparation and rapidity of analysis.

The possibility of direct determination of trace amounts (10^{-9} – 10^{-5} mol litre⁻¹) of heavy metals in water, soil extracts and other natural subjects by the sorption-colouristic method was considered.¹⁴⁴ Coloured zones are produced upon frontal chromatographic sorption of Hg(II), Cd(II), Pb(II), Co(II), Cu(II), Bi(III), Sb(III) and Fe(III) on microcolumns packed with cellulose and polystyrene-based ion-exchange resins modified with polar residues (*e.g.*, sulfides of zinc, cadmium and manganese as well as hexacyanoferrates of calcium and lead) and organic reagents.

3. Foamed polyurethanes and membranes

The polymeric matrix of foamed polyurethanes, which have a membrane structure, contains both polar groups and hydrophobic fragments. This makes foamed polyurethanes helpful tools in test methods for the determination of metal cations, polycyclic hydrocarbons, phenols, heteropolyacids, surfactants and other compounds.^{93, 123, 138, 145}

A number of test reactions on foamed polyurethane carriers have been developed for determination of several elements (the colour scale ranges, Δc , are indicated):

Element	Cr	Ni	Co	Ti	Fe
$\Delta c / \text{mg litre}^{-1}$	0.1–1	0.1–40	0.04–6	0.01–0.5	0.004–0.6

1,5-Diphenylcarbazide and dimethylglyoxime are used for the determination of chromium and nickel, respectively; potassium thiocyanate is used for the determination of cobalt, titanium and iron.⁹³

Immobilisation of chitosan HRP on foamed polyurethane gives a more active and stable sorbent than on a polystyrene plate or on paper. Oxidation of *o*-dianizidine proved to be the most efficient indicator reaction which made it possible to decrease the detection limit for mercury to 25×10^{-3} ng ml^{-1} . The rate of the indicator reaction is monitored visually by fixing the moment of appearance of red-coloured oxidation product. Thiourea was used to enhance the inhibitory effect of mercury. This method is not only highly sensitive, but also highly selective: only 10^5 -fold excess of Cd(II), Pb(II) and Bi(III) interfere with the determination.¹²³

Optimum conditions were established for complexation of uranium(VI) with PAR immobilised on foamed polyurethane,

KU-2 and Silochrom C-120. The detection limit is $0.1 \mu\text{g ml}^{-1}$ (see Ref. 138).

Test methods employing poly(vinyl chloride) and caprone membranes were recommended for the determination of Hg(II), Ag(I), Cu(II), Au(III), Pd(II) and Pt(IV) in the presence of at least a 10-fold excess of Fe(III), Ni(II), Co(II), Zn(II), Cd(II), Be(II), Al(III) and alkaline-earth metals with detection limits from 1 to $15 \mu\text{g litre}^{-1}$. Immobilised azorhodanines and Sulfonitrophenol M were used as reagents.⁸⁵

A highly sensitive field test for the determination of chromium(VI) in water at the level of $< 1 \mu\text{g litre}^{-1}$ is based on the formation of a coloured chromium complex with 1,5-diphenylcarbazide in 0.1 M sulfuric acid and its sorption on an ion-exchanger incorporated into the membrane.¹⁴⁶ The intensity of coloration is proportional to the chromium concentration in the range from 0.05 to $50 \mu\text{g litre}^{-1}$. In 50-ml samples, chromium is determined with a detection limit of 10 ng litre^{-1} .

4. Fibrous materials filled with ion-exchange resins

Fibrous filled materials are perfect carriers for visual assays. They allow for simultaneous concentration and determination of tested elements as well as for variation in the nature of the adsorbent depending on a concrete experimental task. The tested ions may first be adsorbed on original, colourless materials and are then 'developed'. Alternatively, adsorbents with immobilised reagents can be used. Carriers can be used under both static and dynamic conditions; they are resistant to mechanical and chemical actions.

Fibrous materials filled with ion-exchange resins and fabrics with ionogenic groups are used as carriers in visual determinations of metal ions using known colour reactions with organic reagents.^{69, 74, 99, 147–151} The tested element is selectively concentrated on a solid phase; the use of highly sensitive and highly selective reagents facilitates its determination in drinking water at the MPC and lower levels.

In addition to remarkable kinetic properties (*e.g.*, ease of sorption and high filtration rates), fibrous materials endowed with

ion-exchange properties manifest high stabilities in aggressive media. Therefore they can be used for sorption and determination of metal ions under drastic conditions in the presence of large concentrations of masking substances and in highly acidic media. These materials are distinguished by handling convenience, are easily transferred with pincers and do not lose their shape upon stirring, heating in solution, drying, *etc.*

Express tests are based on colour reactions of metal ions with reagents on a solid phase. Fibrous materials filled with ion-exchange resins used as carriers and fabrics with ionogenic groups in the form of discs 1–2 cm in diameter serve not only as the reaction sites but also as sorbents for the concentration of tested ions (and thus increasing the sensitivity of the reaction) and their separation from ballast substances. The use of carriers containing specific groups allows one to lower the detection limit and to increase the selectivity. In addition, these express methods employ well-known, organic reagents that have proved to be efficient in photometric assays and are commercially available which significantly simplifies their introduction into routine analytical practice.

The analytical procedure is simple and easily accessible. Reagent solutions are added dropwise to a tested solution (10 ml) to ensure optimum sorption conditions after which the carrier disc is introduced. The solution is agitated for 5–7 min and then decanted with the disc held back by a glass rod. One to three drops of the reagent solution are dripped onto a colourless unmodified disc and the colouring of the disc is compared with the calibration colour scale obtained under identical conditions. In some cases, the scale, enclosed in a polyethylene film, is preserved for a sufficiently long period of time. Carrier discs can be regenerated with acids and re-used after washing with water. Some characteristics of modern test methods for visual assessment of metal ions utilising fibrous materials filled with ion-exchange resins and fabrics with ionogenic groups are summarised in Table 2.

Table 2. Some characteristics of test methods for the determination of metal ions which utilise fibrous materials as a solid phase.

Ion (I)	Fibre (fabric)	Sorption conditions	Detection conditions	Selectivity factor		Change in disc colour	Colour scale /mg litre ⁻¹	MPC /mg litre ⁻¹	Ref.
				M	[M/I]				
Fe (III)	KU-2	0.1 M HNO ₃	KSCN	Ni	200	white → red	0.1–1	0.3	99
				Co	50				
				Cd	20				
				Zn	10				
				U(VI)	5				
				Cu	2				
Cu(II)	KU-2	0.01–0.05 M HNO ₃	DETC + + EDTA	Cd, Zn, U(VI),		white → yellow	0.05–1	1	99
				Mn(II)	100				
				Fe(III), Ni	50				
				Co	10				
				Bi	5				
Ni(II)	KU-2	pH 5–6	DMG	Cd, Zn	100	white → red	0.1–1	0.1	99
				Bi	10				
				Fe(III), Cu,	5				
Pd(II)	KU-2	0.01 M HNO ₃	NDEA	Ni, Cu,		yellow → red	0.05–0.5	—	77, 147
				Zn, Cd	10 ⁴				
				Co, Rh, Ir	10 ³				
				Fe(III), Au,					
				Pt, Ru	10 ²				
V(V)	AB-17	pH 2.5, 0.05% H ₂ O ₂	PAR, 1 M HCl, 50–60 °C	Ni	500	yellow → violet	0.1–1	0.1	148, 149
				Cu	200				
				Mo, Cr(VI)	50				
				Fe(III)	20				
				V(IV)	2				

Table 2 (continued).

Ion (I)	Fibre (fabric)	Sorption conditions	Detection conditions	Selectivity factor		Change in disc colour	Colour scale /mg litre ⁻¹	MPC /mg litre ⁻¹	Ref.
				M	[M/I]				
Cr(VI)	AB-17	0.01 M H ₂ SO ₄	DPC	W(VI), Cr(III), H ₂ O ₂ > 10 ³ V(V), Zn 500 Ni, Co, Al, Hg, Fe(III) 200 Pb, Cd 100 Cl ⁻ , SO ₄ ²⁻ > 10 ⁴		white → pink	0.01–0.25	0.05	74, 99
Cr(VI) + Cr(III)	AB-17	oxidation of Cr(III) to Cr(VI)		determination of Cr(VI) against Cr(III) and a sum of chromium ions		the same	0.01–0.25	0.05	99
Mo(VI)	AB-17	pH 3–5, C ₆ H ₈ O ₆	Phenyl-fluorone, 0.5 M HCl	Fe(III) 600 Cr(VI) 100 Sn, Zr 20 V(V), Th 10		orange → crimson	0.02–0.4	0.25	149
Th(IV)	AN-31	0.004 M H ₂ C ₂ O ₄ , pH 2	Arsenazo III, 6 M HCl	F ⁻ , PO ₄ ³⁻ > 10 ³ Fe(III) 300 La, Ti 50 Zr 10 U(VI) 5		pink → grey-green	0.01–0.1	—	69
U(VI)	AN-31	pH 6, acetate buffer	Arsenazo I	La, Fe(III) 20 Th, Al 10 Ti(IV) 2 Zr 1		pink → blue	0.1–1	0.05	64, 147
U(VI) + Th(IV)	AN-31	0.01 M NaHCO ₃ , 0.001 M EDTA, pH 9–10	Arsenazo III, 7 M HCl	Th : U 1 : 3–3 : 1 Zr 3		pink → green	0.02–0.24 (sum) 0.01–0.12 (thorium)	—	150
Zn(II)	F(I)	pH 9–10, borate buffer	DT + DETC	Fe(III), Cu, Co, Ni, Pb > 1		orange → crimson	0.1–0.5	1.5	99
Co(II)	F(II)	pH 5–6, acetate buffer	PAN	Fe(III), Mn 100 Cu, Zn 10 Ni 5		orange → green	0.05–0.5	0.1	99

Studies with two or three elements or with one element in different oxidation states are being developed during the past decade. For example, both Cr(VI) and Cr(III) ions can be determined following oxidation of Cr(III) by heating with ammonium persulfate in 0.05 M H₂SO₄ followed by decomposition of the excess of the oxidant by boiling with subsequent sorption of Cr(VI) ions on discs prepared from fibres filled with an anion-exchange resin and their detection with 1,5-diphenylcarbazine, which gives a pink coloration. The solution is divided into two parts one of which is used for the determination of only Cr(VI) ions and the other one, for the determination of both Cr(III) and Cr(VI) ions after which the concentration of Cr(III) ions is determined from the difference between the two measurements.⁹⁹

If uranium(VI) and thorium(IV) are present in solution in 1 : 3 to 3 : 1 ratios, they can be determined in the same sample with Arsenazo III in the presence of a 3-fold excess of zirconium. Sorption is performed from a carbonate medium in the presence of ethylenediaminetetraacetic acid; the assay is carried out after acidification with 6–7 M HCl. The overall concentration of uranium and thorium is determined judging from the coloration of wet discs; thorium is determined judging from the coloration of dried discs. The coloration of the uranium complex with Arsenazo III disappears upon drying due to a decrease in acidity.¹⁵⁰

V. Conclusion

At present, the detection limits for metal ions attainable using sorption-spectroscopic and test methods reach 10⁻³–10⁻² mg litre⁻¹. Enzymic test methods provide an exception,

for they allow measurements of up to 10⁻⁵ mg litre⁻¹. However, by reason of high complexity of these reactions, the reproducibility of experimental results is rather low. In some cases, sorption-spectroscopic methods allow for a detection limit of 10⁻⁴ mg litre⁻¹.

As can be judged from the increasing number of publications, these methods are extensively developing along several different lines. The range of tested elements and carriers is expanding and novel procedures for the detection of analytical signals (*e.g.*, colorimetry, derived photometry, flow-injection analysis, *etc.*) evolve. New steps are having made on the road to multielement assays.

The equipment for sorption-spectroscopic assays is also being improved. The use of small-size instruments allows a more objective estimation of experimental results, on the one hand, though this increases the cost of assays on the other hand. Test methods intended for routine and versatile uses present particularly great interest in those cases where the most reliable tool is the human eye, especially because sometimes it detects differences in colour much better than any device. In this context, the simplest, easiest, highly contrasting and safe systems provide the most efficient test methods. Sometimes, the sensitivity and accuracy of sorption-spectroscopic methods is one order of magnitude higher than those of test methods. When these methods are used simultaneously, the concentration of toxic elements can be assessed by test methods; more accurate concentration measurements are accomplished by sorption-spectroscopic methods.

Modern test methods allow detections at the MPC level. Some ions, *e.g.*, mercury, selenium, cadmium, *etc.*, having detection

limits below 10^{-3} mg litre $^{-1}$ present a problem. However, the main problem involved in sorption-spectroscopic and test methods is selectivity. In order to increase selectivity, one should make the carrier resistant to aggressive media, such as acids, alkalis, masking complexing compounds, oxidants and reducing agents used to eliminate the interfering effects of ballast components. There must also be a possibility to vary the nature of the carrier in order to increase the sorption of the tested ions and to prevent the sorption of ballast components.

In our opinion, ion-exchange materials have indisputable advantages over paper, membranes, silica gel and other materials. They are characterised by high mechanical and chemical stabilities, high capacity and good kinetic properties, which allows for a significant decrease in the detection limit by increasing the volume of the tested solution in those cases where the sensitivity of a colour reaction is not high enough. The array of active ionogenic groups is rather broad.

The use of fibrous ion-exchange materials eliminates such disadvantage of ion-exchangers as friability and ensures easy drying, washing and other procedures without any detriment to the carrier surface. This increases the reproducibility of experimental results and simplifies the automation of analysis. The use of fibrous materials filled with ion-exchange resins permits one to combine selective concentration of an element with its selective determination and thus solves the problem of selectivity, lowering of the detection limit and rapidity of analysis. In this sense, too, these materials hold much promise.

Recent trends in the development of sorption-spectroscopic and test methods are towards further improvement of assay methodology and synthesis of novel reagents and updating of the existing ones aimed at their use in combination with the solid phase. Some reagents often lose their ability to form complexes upon immobilisation on the carrier. The broadening of the range of carriers and their potentials, variation of the nature and degree of dispersion and filling of carriers may help to solve numerous problems connected with the increase in the sensitivity and selectivity of analytical methods. And, finally, it is necessary to update the existing mini-instruments and to design new ones including those which utilise fibre optics, flow-through cells and mini-computers providing for rapid analysis in an automated regime. This will favour progress in the design of sorption-spectroscopic and test methods and their application in the analysis of natural and industrial materials and environmental subjects.

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^a — *Russ. J. Anal. Chem. (Engl. Transl.)*

^b — *Moscow Univ. Bull. (Engl. Transl.)*

^c — *Russ. Chem. Bull. (Engl. Transl.)*

^d — *Russ. J. Inorg. Chem. (Engl. Transl.)*

Naphthyridines. Structure, physicochemical properties and general methods of synthesis

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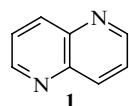
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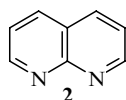
Abstract. Data on the synthesis, chemical properties and applications of naphthyridines published mainly over the last 15 years are described systematically and analysed. The bibliography includes 238 references.

I. Introduction

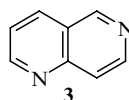
Naphthyridines (pyridopyridines, diazanaphthalenes) represent a group of six isomeric heterocyclic systems containing two fused pyridine rings with different mutual arrangements of nitrogen atoms. They include two groups of compounds — N(1),N(*i*)-naphthyridines (*i* = 5, 6, 7, 8) **1–4** and N(2),N(*j*)-naphthyridines (*j* = 6, 7) **5, 6**.



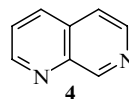
1,5-naphthyridine



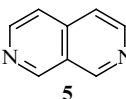
1,8-naphthyridine



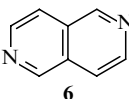
1,6-naphthyridine



1,7-naphthyridine



2,7-naphthyridine



2,6-naphthyridine

The first derivative of the cyclic naphthyridine system was obtained in 1893 by Reissert,¹ who proposed this name for the new class of heterocyclic compounds. The first representatives of unsubstituted naphthyridines — 1,5-naphthyridine **1**² and 1,8-naphthyridine **2**³ — were described only in 1927. Naphthyridines containing nitrogen atoms at positions 1,6 (**3**),⁴ 1,7 (**4**),⁵ and 2,7 (**5**)⁶ were prepared in 1958, and 2,6-naphthyridine (**6**)^{7,8} was synthesised only in 1965. Since then, researchers have shown ever increasing interest in the chemistry of naphthyridines. Indeed, the bibliography of a review⁹ published in 1950 included 75 references, while that of a review¹⁰ which appeared in 1970

comprised 242 references. More recent reviews^{11,12} (1983) present 223 studies. Several reviews dealing with more specific aspects were also published before 1983.^{13–22} In recent years, the number of publications devoted to various aspects of naphthyridine chemistry has sharply increased. More than 1000 publications have appeared during the last 15 years, 40% of them being patents.

This interest in naphthyridine derivatives is due to the exceptionally broad spectrum of their biological activities. They are used for the diagnostics and therapy of diseases of humans including AIDS; for combating exo- and endo-parasites in agriculture and in cattle breeding; as preservatives and ingredients of cutting fluids, as ligands in analytical chemistry, etc.

This review mainly surveys the data published over the last 15 years; however, earlier fundamental studies are also invoked in the discussion of structures, physicochemical properties and reactivities of naphthyridines.

II. Physicochemical properties

1. Structure

X-Ray diffraction study was first performed for unsubstituted 1,5- (**1**) and 2,6-naphthyridines (**6**).^{10,23,24} It was found that transition from pyridine to naphthyridines is accompanied by shortening and lengthening of C–C bonds approximately equal to that observed on passing from benzene to naphthalene. In addition, the N–C bonds in naphthyridines were found to be shorter than these bonds in pyridine. X-Ray diffraction analysis was also used to determine the structures of several naphthyridine derivatives, **1**, **2**, **4** and **6**.^{25–37}

2. Quantum-chemical calculations

Since the 1950s, quantum chemistry methods have been used to elucidate structure–property relationships in the naphthyridine series.^{38–57} The intensities of bands in the UV spectra of naphthyridines have been found to be correlated with the energies of lower unoccupied molecular orbitals;^{38–40} quantum-chemical calculations have also been used in the ¹H and ¹³C NMR spectroscopy^{47–51} and for comparison of the total π -energy and delocalisation energy for naphthyridines and naphthalene.^{41,43} Other results include determination of π -electron distribution;^{43,44} elucidation of correlations of the total π -electron energy with specific features of electrophilic⁴³ and nucleophilic^{43,44} substitution and with the hyperfine splitting constants in the EPR spectra.⁴⁷

In recent years, quantitative structure–biological activity relationships for 6-[2-(4-arylpiperazino)ethyl]-5,6,7,8-tetrahydro-

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1,6-naphthyridines have been established⁵³ and complexes of antitumour antibiotics — naphthyridinomycins — with DNA have been studied by molecular modelling methods.⁵⁴

3. Spectroscopy

Spectroscopic techniques (UV, IR, ¹H and ¹³C NMR) are widely used not only to identify naphthyridines but also to elucidate fine points concerning their structures.^{10, 12}

Thus it has been found that the UV spectra of 1,5-, 1,6-, 1,7- and 1,8-naphthyridines **1–4** are fairly similar to one another and contain three separate groups of bands, analogous to the bands displayed in the spectra of quinoline and isoquinoline. However, the spectra of 2,7- and 2,6-naphthyridines **5** and **6** differ both from each other and from the spectra of any other naphthyridines.^{10, 58} The UV spectra of 4-hydroxy-1,5-naphthyridine⁵⁹ and of a large number of substituted 1,8-naphthyridines⁶⁰ have been analysed in detail. In order to disclose the influence of substituents on the absorption spectra, UV spectra of 1,8-naphthyridines monosubstituted at position 2 (Me, Cl, Br, OMe, OEt, SMe, NH₂, OH, SH), position 3 (Me, Cl, Br, NO₂, NH₂) and position 4 (Me, Cl, Br, OMe, OEt, OH, SH) have been studied.⁶¹

Transmission and absorption spectra of 1,8-naphthyridine **2** in the range of 50 000–20 000 cm^{−1} have been investigated in solutions and in various mixed crystals at 4.2 and 300 K.⁵² The pattern of the band corresponding to the $\pi \rightarrow \pi^*$ transition was found to be similar to that observed in the spectrum of the related naphthalene molecule with allowance for perturbations induced by the replacement of carbon by nitrogen. The position of the long-wavelength $\pi \rightarrow \pi^*$ band at about 27 000 cm^{−1} complies with the theoretical predictions based on extended Hückel calculations. The bands at about 31 600–31 900 cm^{−1} were assigned empirically to the second $n \rightarrow \pi^*$ transition.⁵²

All bands in the IR spectra of several substituted 1,5-naphthyridines have been assigned; the spectrum of 1,5-naphthyridine **1** was compared with the spectrum of 5-substituted quinoline.⁶² IR spectroscopy was used to study the keto–enol tautomerism of 4-hydroxy-1,5-naphthyridine in solution and in the solid state; it was found that the keto form predominates in polar solvents and the enol form, in nonpolar solvents.⁵⁹

Study of the IR and Raman spectra of 1,6- and 1,8-naphthyridines permitted the assignment of all 42 fundamental vibrations of these two heterocyclic systems.⁶³

Data on the ¹H NMR spectra (chemical shifts and spin–spin coupling constants) for the naphthyridines **1–4** and **6** can be found in the literature.^{7, 8, 10, 12, 42, 43, 49–51, 64–77} The chemical shifts observed in the ¹³C NMR spectra of the naphthyridines **1–6** were compared with those for quinoline and isoquinoline.^{12, 49–51} The resonance signals in the ¹H NMR spectrum of 2-(2'-pyridyl)-1,8-naphthyridine were completely assigned using homonuclear 2D NMR spectroscopy.⁷⁵

The behaviour of derivatives of the isomeric naphthyridines **1–4** under electron impact has been studied and the main fragmentation pathways have been identified.^{10, 78–80} The structures and destruction pathways of the isomeric ions [M–HCN]^{−•} and [M–2 HCN]^{−•}, resulting from fragmentation of the naphthyridines **1–4** and benzazines, were studied using collisional activation.⁸¹ It was found that the [M–2 HCN]^{−•} ions can exist as two isomers, one of them being characteristic of naphthyridines and the other being characteristic of benzazines.

High-resolution photoelectron spectra of the naphthyridines **1–6** have been described.⁸² The ionisation potentials for the n and π orbitals are listed in Table 1.

Polarised phosphorescence spectra of 1,5-naphthyridine **1**^{83–85} and the EPR spectrum of 1,6-naphthyridine **3** were recorded.⁸⁶

A number of publications deal with the capacity for ionisation (including the pK_a values) of the naphthyridines **1–4** and their derivatives.^{10, 58, 70, 87–91}

Table 1. Ionisation potentials (eV) of naphthyridines **1–6**.⁸²

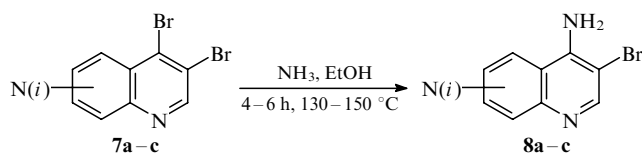
Compound	n -Orbital	π -Orbital
1,5-Naphthyridine 1	9.20	11.05
	10.40	
	1.20	
1,8-Naphthyridine 2	9.20	11.33
	10.10	
	0.90	
1,6-Naphthyridine 3	9.50	9.07
	9.90	
	0.40	
1,7-Naphthyridine 4	9.30	8.99
	10.00	
	0.70	
2,7-Naphthyridine 5	9.35	8.98
	10.10	
	0.75	
2,6-Naphthyridine 6	9.40	8.87
	10.00	
	0.75	

III. The reactivity of naphthyridines

Reactions of naphthyridines including electrophilic substitution (bromination, nitration), nucleophilic substitution (amination, metallation), reduction, oxidation, complexation, *etc.*, have been considered fairly comprehensively in reviews.^{10, 12} In yet another review, attention is focussed on the reactivity of naphthyridines towards N-nucleophiles.¹¹ Here we survey the data on the reactivity of naphthyridines published over the last 15 years.

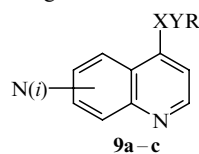
Electrochemical reduction of the naphthyridines **1–6** has been reported.^{92, 93} On exposure to UV radiation in the presence of sodium nitrite, 3-amino-1,6-naphthyridine-4(1*H*)-one eliminates a nitrogen molecule being thus converted into 5-azaindole-3-carboxylic acid.^{94, 95}

Nucleophilic substitution of bromine at position 4 in 3,4-dibromonaphthyridines **7a–c** on treatment with a saturated alcoholic solution of ammonia in an autoclave affords 4-amino-3-bromo-N(1),N(*i*)-naphthyridines **8a–c**.⁹⁶



$i = 5$ (**a**), 6 (**b**), 7 (**c**).

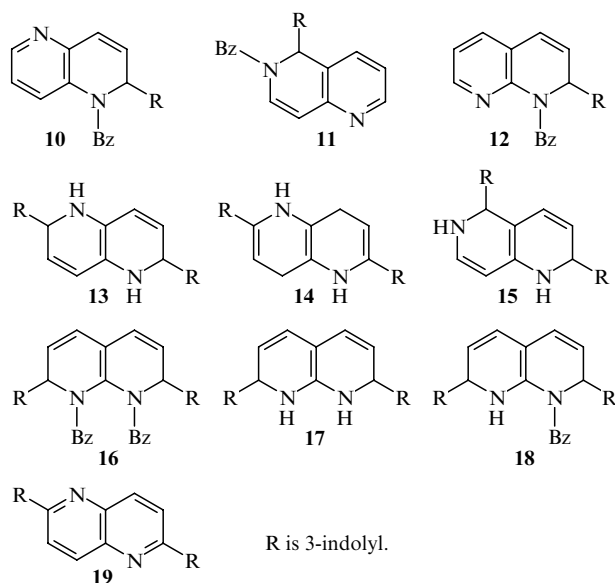
The naphthyridine derivatives **9a–c**, possessing fungicidal activity, have been synthesised using nucleophilic substitution of the halogen atoms in isomeric halo naphthyridines. These products can also be employed for combating exo- and endo-parasites in agriculture and cattle breeding, for wood protection, and as preservatives for paints, varnishes and cutting fluids during metal working.⁹⁷



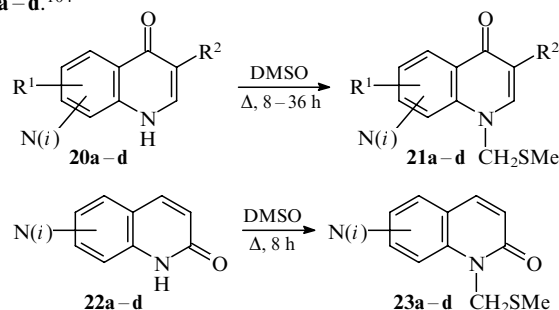
$i = 5$ (**a**), 6 (**b**), 7 (**c**); X = O, S, SO, SO₂; Y is alkenyl or a single bond; R is cycloalkyl or piperidin-2-yl.

In recent years, nucleophilic addition reactions have been widely used for the synthesis of various derivatives of isomeric naphthyridines. For example, nucleophilic addition of indole to 1,5-, 1,6- and 1,8-naphthyridine derivatives in the presence of

benzoyl chloride in toluene or DMF yields, depending on the temperature and reactant ratio, hydrogenated mono- (**10**–**12**) or bis-(3-indolyl)naphthyridines **13**–**18**.^{98–100} Hetarylation includes the *in situ* formation of *N*-acyl heteroaromatic cations and the addition of nucleophiles to them. Aromatisation of the *N*-acylated hydrogenated naphthyridine derivatives **13** and **14** on treatment with tetrachloroquinone affords the same compound, naphthyridine **19**.

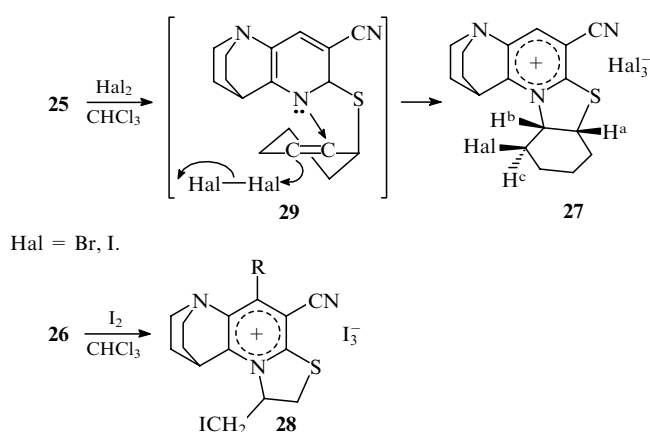
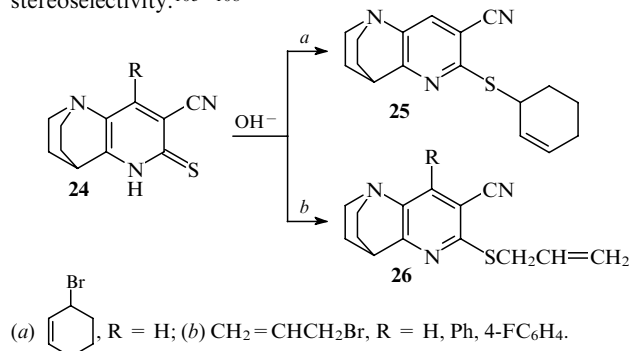


Refluxing of *N*(1),*N*(*i*)-naphthyridin-4(1*H*)-ones **20a–d** in DMSO gives rise to 1-methylthiomethyl naphthyridine derivatives **21a–d**, which depress microbial growth.^{100–103} Similar methylthiomethylation of naphthyridin-2(1*H*)-ones **22a–d** has resulted in *N*-substituted *N*(1),*N*(*i*)-naphthyridin-2(1*H*)-ones **23a–d**.¹⁰⁴



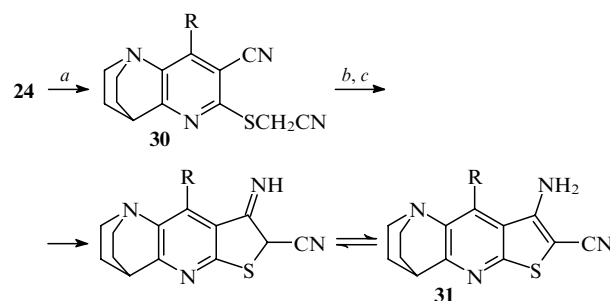
i = 5 (**a**), 6 (**b**), 7 (**c**), 8 (**d**); R^1 = H, Me; R^2 = H, CO₂H, CO₂Et.

Regioselective alkylation of quinuclidinopyridine-2(1*H*)-thiones **24**, containing a 1,5-naphthyridine fragment, with 3-bromocyclohexene or allyl bromide in the presence of a base affords the corresponding 2-(cyclohex-2-enylthio)- (**25**) and 2-allylthio-derivatives **26**. Halogen-induced quaternisation of these products is a synchronous process yielding salts **27** and **28** with high regio- and stereoselectivity.^{105–108}



X-Ray diffraction analysis has shown that the pyridine nitrogen atom in the compound **25** has a short non-valence contact with the C=C bond of the cyclohexene fragment. The close arrangement of these reaction sites is favourable for synchronous cyclisation in intermediate **29** involving the H^a, H^b and H^b, H^c systems of protons. The high stereoselectivity of this reaction is apparently due to the synchronism of the action of the donor (*i.e.* the lone electron pair of the naphthyridine nitrogen atom) on the π -electrons of the cyclohexene double bond and electrophilic rupture of the double bond, which are followed by quaternisation. Thus the H^b and H^c protons occupy *trans*-positions. This intramolecular electrophilic quaternisation of the compound **25** can be regarded as synchronous *trans*-quaternisation with *cis*-annulation.¹⁰⁸

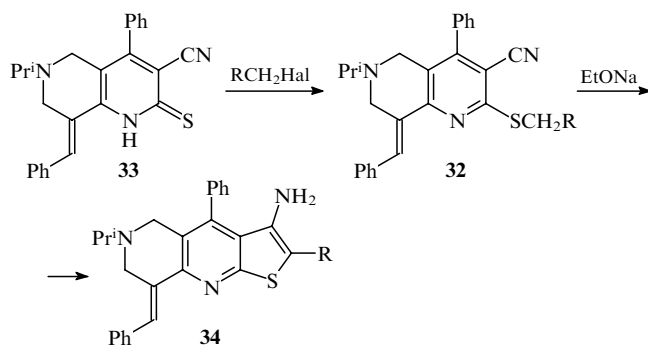
2-Cyanomethylthio derivatives **30**, prepared by alkylation of the compounds **24** with chloroacetonitrile, cyclise under conditions of the Thorpe–Ziegler reaction to give the corresponding thieno[2,3-*b*]pyrido[3,2-*e*]quinuclidines **31**, containing a 1,5-naphthyridine fragment.¹⁰⁷



R = H, Ph, 4-FC₆H₄;

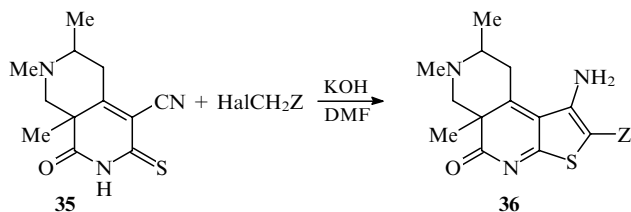
(a) ClCH₂CN, KOH, DMF, 25 °C, 3 h; (b) OH[−]; (c) H⁺.

Similar treatment with sodium ethoxide of thioethers **32**, prepared by the reaction of 1,2,5,6,7,8-hexahydro-1,6-naphthyridine-2-thiones with halo ketones, esters, amides or nitriles, resulted in the synthesis of thieno[2,3-*b*]-1,6-naphthyridines **34**.¹⁰⁹



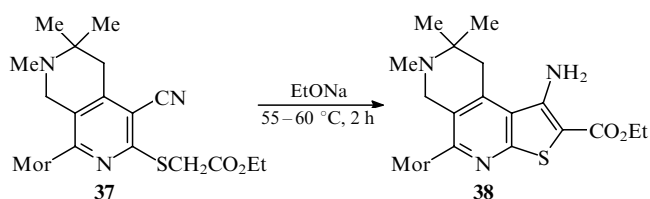
R = MeCO, PhCO, EtO₂C, CONH₂, CONHPh, CN, CONHC₆H₄Me-4, CONHC₆H₄OMe-4, CONHC₆H₄COMe-4.

The reaction of 6,7,8*a*-trimethyl-1-oxo-3-thio-1,2,3,5,6,7,8,8*a*-octahydro-2,7-naphthyridine-4-carbonitrile (**35**) with 4-bromophenacyl bromide or *N*-cyanochloroacetamide in the presence of a base gives thieno[2,3-*c*]-2,7-naphthyridines **36**.¹¹⁰



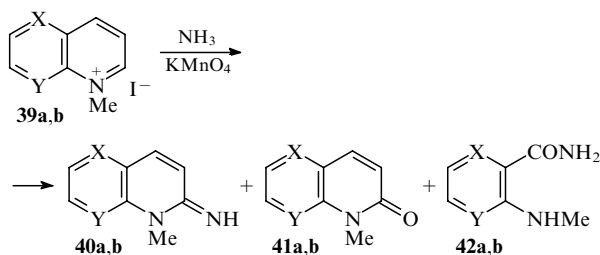
Hal = Br, Z = 4-BrC₆H₄CO; Hal = Cl, Z = C(NH₂)NCN.

Cyclocondensation of 3-ethoxycarbonylmethylthio-2,7-naphthyridine **37** on heating in anhydrous ethanol in the presence of an equimolar amount of sodium ethoxide affords thienonaphthyridine **38**. The dihydrochloride of the compound **38** possesses a mutagenic activity.¹¹¹



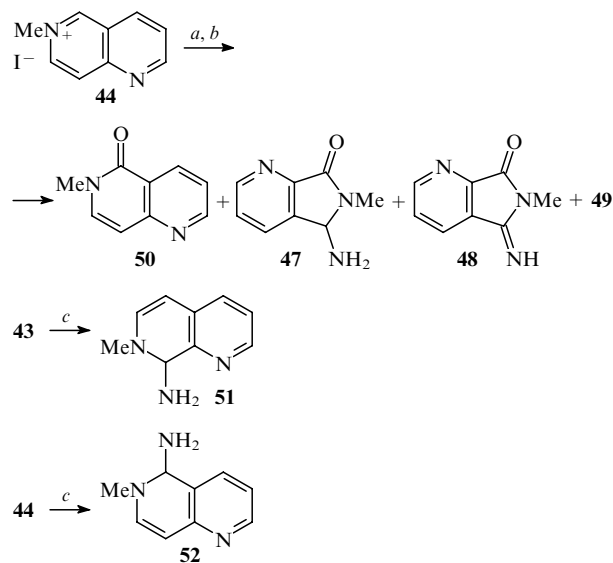
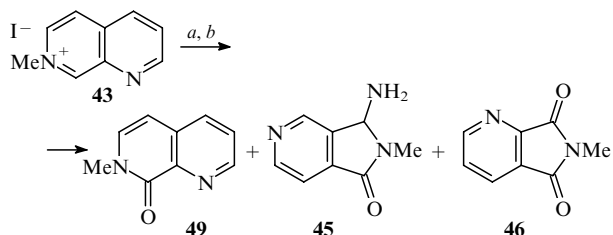
Mor is morpholin-1-yl.

Treatment of 1-methyl-N(1),N(*i*)-naphthyridinium iodides **39a,b** with liquid ammonia in the presence of potassium permanganate gives rise to mixtures of imino (**40a,b**) and oxo (**41a,b**) derivatives of dihydronaphthyridines and vicinal methylamino-pyridinecarboxamides **42a,b**.¹¹²



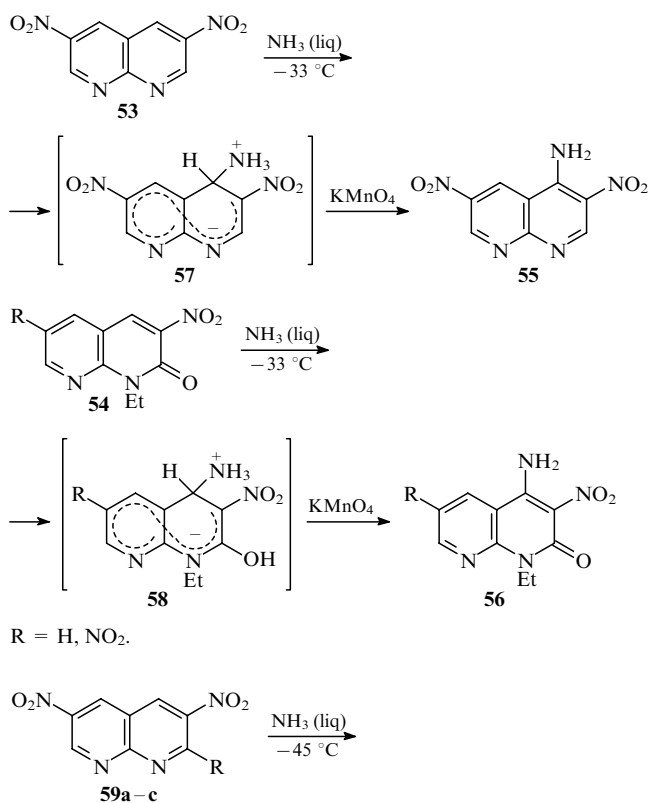
X = N, Y = CH (a); X = CH, Y = N (b).

Unlike compounds **39a,b**, 7-methyl-1,7-naphthyridinium iodide **43** and 6-methyl-1,6-naphthyridinium iodide **44** react with liquid ammonia and KMnO₄ with ring contraction as the predominant reaction pathway yielding 4-azaindole derivatives **45–48** together with the oxo derivatives of the corresponding dihydronaphthyridines **49** and **50**. Study of the ¹H NMR spectra showed that on treatment with liquid ammonia in the absence of potassium permanganate, the compounds **43** and **44** are converted into amino derivatives **51** and **52**.¹¹³

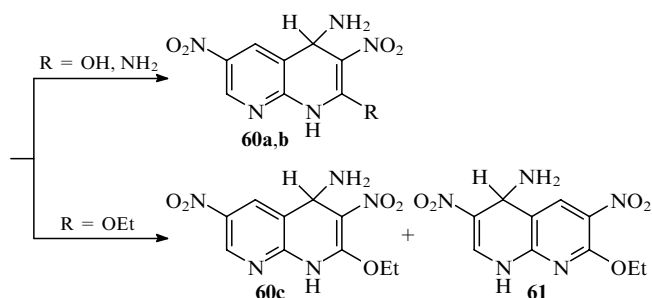


(a) NH₃ (liq), KMnO₄, –33 °C; (b) OH[–]; (c) NH₃ (liq).

When 3,6-dinitro-1,8-naphthyridine **53** or 6-*R*-1-ethyl-3-nitro-1,8-naphthyridin-2(1*H*)-ones **54** are made to react with a solution of potassium permanganate in liquid ammonia at –33 °C, amination proceeds giving rise to the corresponding 4-amino derivatives **55** and **56**. The intermediate formation of σ -adducts **57** and **58** was detected by ¹H NMR spectroscopy.^{114,115} It was also shown that 1-ethyl-3-nitro-1,8-naphthyridin-4-one is not aminated under these conditions.¹¹⁵ However, treatment of 1,8-naphthyridine derivatives **59a,b** with liquid ammonia at –45 °C affords 4-amino-1,4-dihydro-3,6-dinitro-2-*R*-1,8-naphthyridines **60a,b**. The compound **59c** was converted into a mixture of the naphthyridine **60c** and isomeric 5-amino-2-ethoxy-3,6-dinitro-5,8-dihydro-1,8-naphthyridine **61**.¹¹⁶

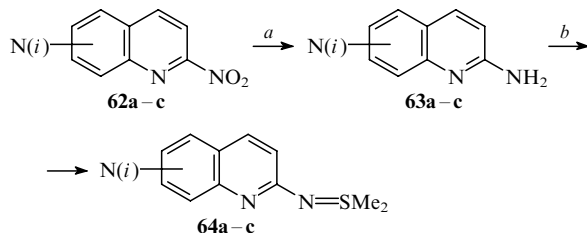


R = H, NO₂.



$R = OH$ (a), NH_2 (b), OEt (c).

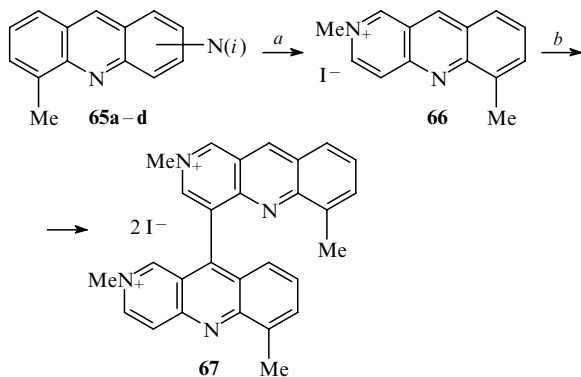
2-Nitro-N(1),N(i)-naphthyridines **62a-c** undergo replacement of the nitro group rather than amination on treatment with a solution of potassium permanganate in liquid ammonia; this gives the corresponding 2-aminonaphthyridines **63a-c**, although their yields are relatively low. These products react with DMSO and trifluoromethanesulfonic anhydride giving rise to *S,S*-dimethyl-[N(1),N(i)-naphthyridin-2-yl]sulfylimines **64a-c**.¹¹⁵



$i = 5$ (a), 6 (b), 8 (c);

(a) NH_3 (liq), $KMnO_4$, $-33^\circ C$; (b) DMSO, $(CF_3SO_2)_2O$.

The kinetics of *N*-methylation of benzonaphthyridines **65a-d** with methyl iodide in DMSO have been studied.¹¹⁷ It was shown that the salt **66**, formed from the naphthyridine **65b**, slowly dimerises in a 10% aqueous solution of DMSO to give compound **67**.

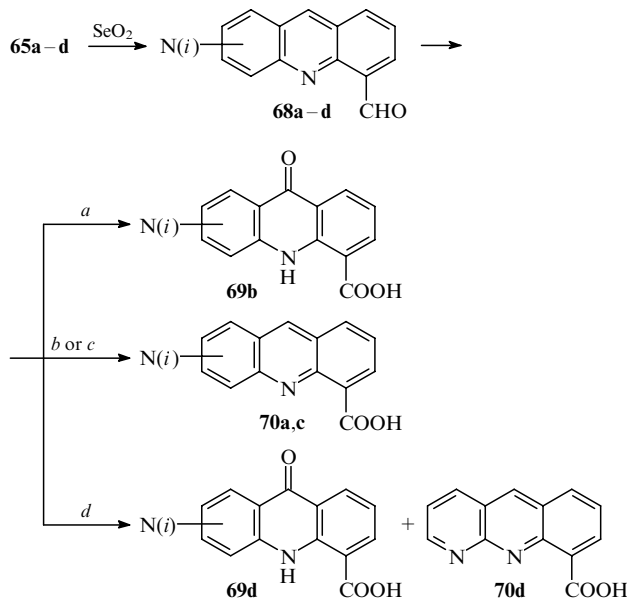


$i = 5$ (a), 6 (b), 7 (c), 8 (d);

(a) $i = 6$, MeI, $MeCO_2Et$, Δ , 0.5 h; (b) DMSO– H_2O (1:9), 10 h.

The methyl group in benzo[2,3]naphthyridines **65a-d** can be easily modified. Thus refluxing of these compounds with SeO_2 in chloro-, 1,2-dichloro- or 1,2,4-trichlorobenzene gives aldehydes **68a-d**, which serve as the starting compounds for the synthesis of diverse functional derivatives of benzonaphthyridines.^{118–120} Oxidation of the compounds **65a-d** to the aldehydes **68a-d** and further oxidation to the corresponding acids are the key stages of the synthesis of compounds **71–75**, which are the aza analogues of

the potential antitumour preparation, *N*-[2-(dimethylamino)-ethyl]acridine-4-carboxamide.^{118–120}



$i = 5$ (a), 6 (b), 7 (c), 8 (d); (a) $i = 6$, $NaClO_2$; (b) $i = 7$, Ag_2O ; (c) $i = 5$; (d) $i = 8$, $NaClO_2$.

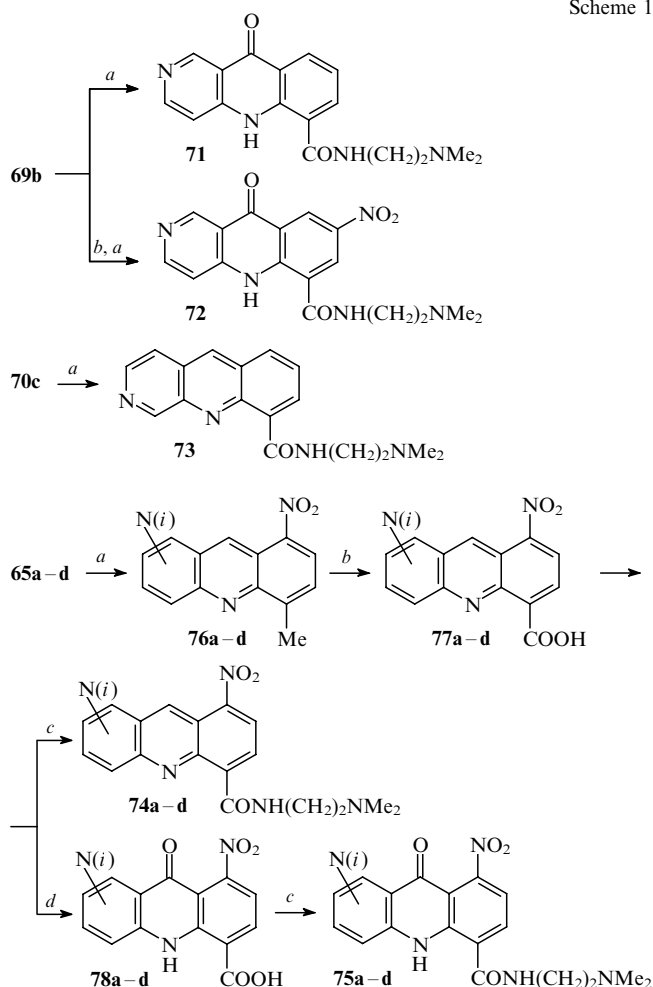
The aldehydes **68a-d** can be oxidised using Ag_2O , $NaClO_2$, $K_2Cr_2O_7$, etc.; oxidation can proceed to different extents depending on the structure of the initial compound and the reagent employed. For instance, oxidation of the aldehyde **68b** with $NaClO_2$ involves the central ring and gives oxo acid **69b**. The oxidation of the aldehyde **68c** with Ag_2O affords acid **70c** as the only product. The aldehyde **68a** is oxidised by Ag_2O to **70a** but the reaction does not proceed to completion, up to 10% of the starting compound being recovered unchanged. The reaction of the aldehyde **68d** with $NaClO_2$ yields a mixture of acids **69d** and **70d**. The oxo acids **69a-d** are also produced upon oxidation of **68a-d** with $NaClO_2$ in Bu^iOH .

Further modification of the acids **69** and **70** includes reactions of the carboxy group with 2-(*N,N*-dimethylamino)ethylamine and nitration of the benzene ring. Thus compounds **74** and **75** were prepared by oxidation of the methyl group in nitro derivatives **76** followed by modification of the acids **77** and **78** formed (Scheme 1).

Dipolar 1,3-cycloaddition of various dienophiles to benzo[3,4]naphthyridinium ylides **79–81**, generated *in situ* by dehydrobromination of the corresponding quaternary salts, has been studied; this gives rise to benzo[*h*]pyrrolonaphthyridines **82–88** (Scheme 2).^{121–126} The compounds **82–84** exhibit bactericidal activities.^{124, 125}

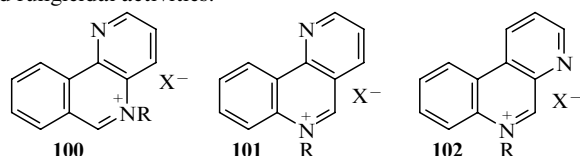
The dipolar 1,3-cycloaddition of *N*-dichloromethylides **89–91**, generated *in situ* from the corresponding benzo[*h*]naphthyridines **92–94** and dichlorocarbene¹²⁷ (produced from CCl_3CO_2Na on heating or from $CHCl_3$ in the presence of a base and $Et_3BnN^+Cl^-$), to dimethyl acetylenedicarboxylate is less selective; only the ylide **89** is converted into the corresponding adduct **95** in 52% yield. In the case of **90** and **91**, the reaction gives a mixture of dipolar 1,3-addition products **96** and **97** and bisadducts **98** and **99** (Scheme 3). Quaternisation of naphthyridines **92–94**^{128–130} (the compounds **92** and **93** were prepared by the Skraup method¹²⁸ and **94** was synthesised by photocyclisation of diazastilbene¹³¹) induced by alkyl, aryl or benzyl halides gave

Scheme 1



(a) KNO_3 , H_2SO_4 ; (b) $\text{K}_2\text{Cr}_2\text{O}_7$, H_2SO_4 ; (c) $\text{Me}_2\text{N}(\text{CH}_2)_2\text{NH}_2$; (d) NaClO_2 .

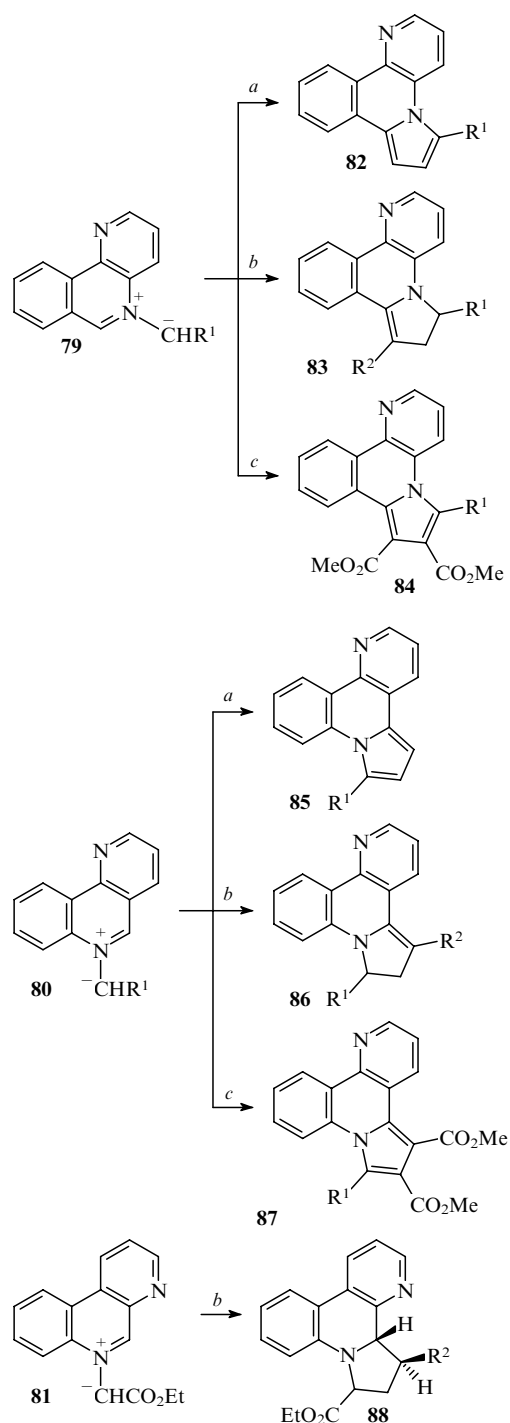
quaternary salts **100–102**. The salts **101**, **102** exhibit bactericidal and fungicidal activities.¹²⁸



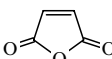
$\text{R} = 2,4\text{-(NO}_2)_2\text{C}_6\text{H}_3$, $\text{H}_2\text{C=CHCH}_2$, Bn , $\text{Me}(\text{CH}_2)_9$; $\text{X} = \text{Cl}$, I .

In order to elucidate the influence of the structure of benzo[*h*]-naphthyridines on their reactivity, charge distributions, excitation energies, and the oscillator strengths for the molecules **92–94** and their amino derivatives have been calculated. The calculation was carried out by a semiempirical self-consistent field method in the Pariser–Parr–Pople π -electron approximation with allowance for the configurational interaction between singly excited states and by the Hückel method. The results are in satisfactory agreement with the data of the UV spectra.¹³² The populations of the atomic π -orbitals, the order of π -bonds and the frequency and oscillator strengths for three electron transitions in the molecules of the naphthyridines **92–94** and their salts **100–102** were also calculated. By comparing the calculated and experimental spectra, correlation coefficients for the relation $\nu_{\text{calc}} = a\nu_{\text{exp}} + b$ were determined.¹³³

Scheme 2



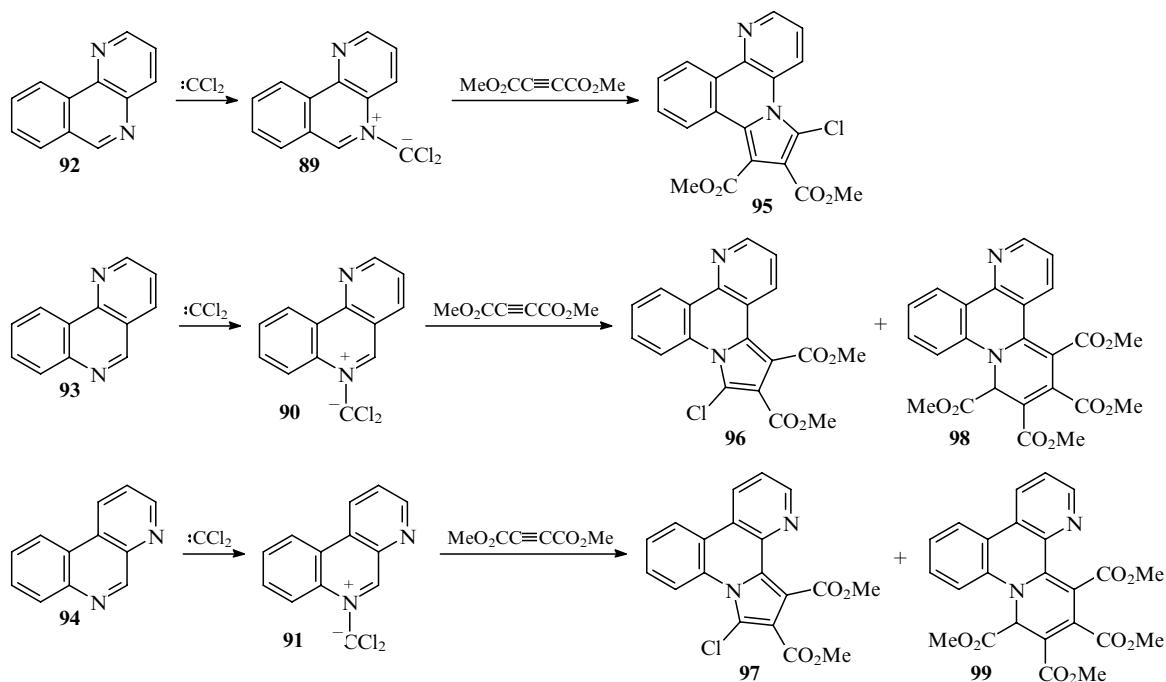
$\text{R}^1 = \text{COPh}$, CO_2Et ; $\text{R}^2 = \text{CN}$, CO_2Et , Ac ;

(a) ; (b) $\text{CH}_2=\text{CHR}^2$; (c) $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$.

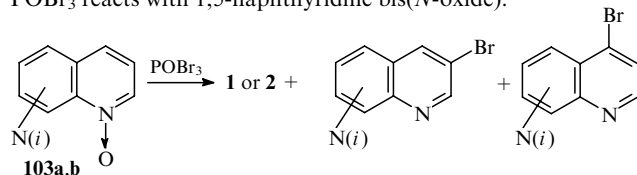
The formation of *N*-ylides of the benzonaphthyridinium series upon dipolar 1,3-addition of benzonaphthyridine *N*-oxides to dimethyl acetylenedicarboxylate at room temperature has been reported.¹³⁴

Treatment of *N*-oxides **103a,b** with POBr_3 affords a mixture of 1,5- (**1**) or 1,8-naphthyridines (**2**) with their brominated deriva-

Scheme 3

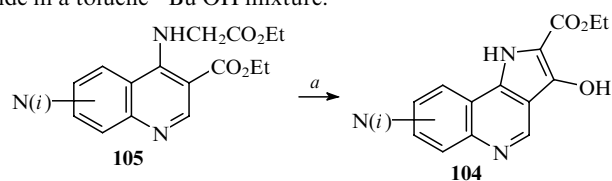


tives. A similar mixture of reaction products is also formed when POBr_3 reacts with 1,5-naphthyridine bis(*N*-oxide).¹³⁵



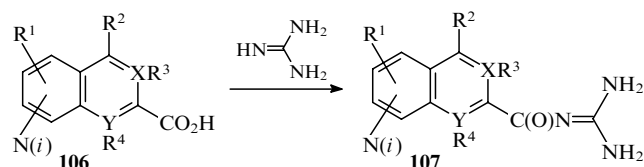
$i = 5$ (a), 8 (b).

Carboxylic acid derivatives **104** of the pyrrolonaphthyridine series — potential preparations for treatment of degenerative, ischemic, and autoimmune diseases — have been synthesised using intramolecular cyclisation of ethyl (3-ethoxycarbonylnaphthyridin-4-ylamino)acetates **105** induced by potassium *tert*-butoxide in a toluene– Bu^tOH mixture.¹³⁶



(a) Bu^tOK , PhMe, Bu^tOH , 20 h.

The reaction of naphthyridinecarboxylic acids **106** with guanidine in the presence of carbonyldiimidazole in anhydrous THF results in heteroylguanidines **107**, which can be used for the therapy of heart diseases, for surgical operations and organ transplantation, for the diagnostics and treatment of hypertension and proliferative diseases.¹³⁷



$\text{R}^1, \text{R}^2 = \text{H}, \text{Hal}, \text{Alk}, \text{alkenyl}, \text{alkynyl}, \text{CN}, \text{AlkF}$;
 $\text{R}^3, \text{R}^4 = \text{H}, \text{Hal}, \text{Alk}, \text{AlkF}, \text{AlkO}, \text{Alk}_2\text{N}, \text{CON}=\text{C}(\text{NH}_2)_2$ or none;
 $\text{X} = \text{N}, \text{Y} = \text{C}; \text{X} = \text{C}, \text{Y} = \text{N}$.

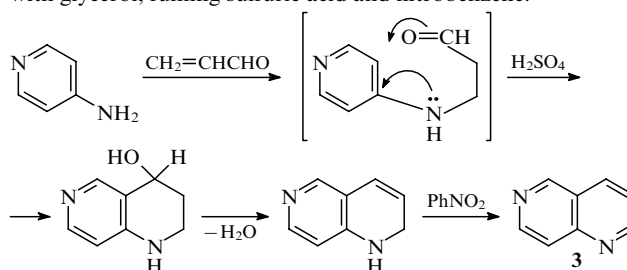
IV. General methods for the synthesis of naphthyridines

General synthetic methods used to prepare various types of naphthyridine include the Skraup, Friedlander and some other name reactions; cyclisation, cyclocondensation, dimerisation reactions, *etc.*

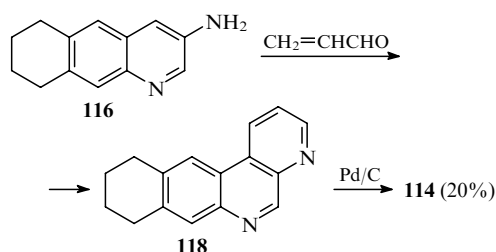
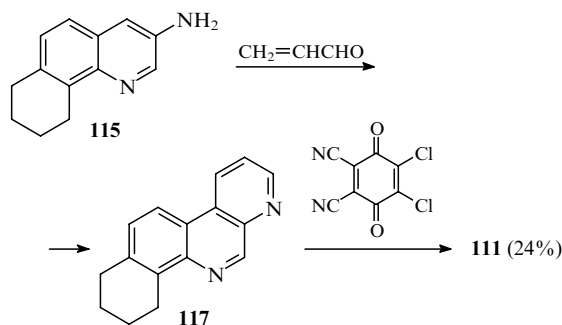
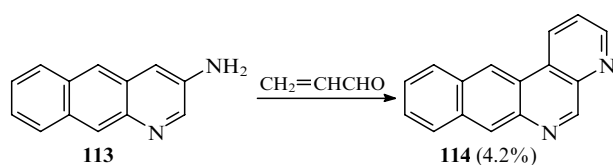
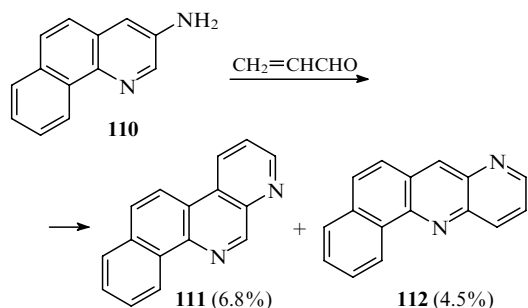
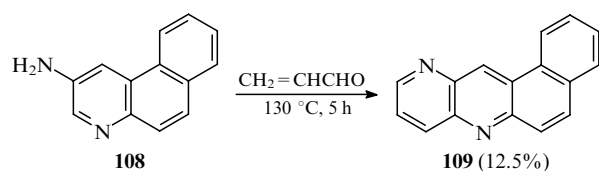
1. The Skraup method and its modifications

The Skraup reaction was first employed to synthesise unsaturated 1,5-naphthyridine **1** from 3-aminopyridine in the late 1920s.^{2, 138, 139} Subsequently this reaction and its modifications have been successfully used to prepare other naphthyridines and their derivatives.^{9, 10, 12}

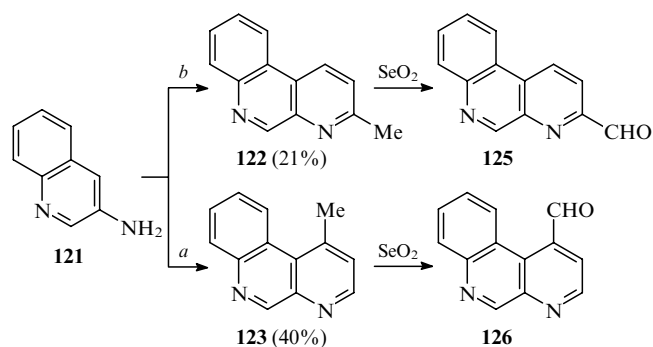
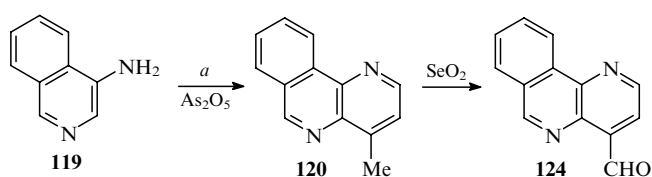
Recently 1,6-naphthyridine **3** has been prepared by the Skraup method, namely, by heating (135°C , 48 h) of 4-aminopyridine with glycerol, fuming sulfuric acid and nitrobenzene.¹⁴⁰



In recent years, a modified Skraup reaction (20% oleum, nitrobenzene, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_3BO_3) has been used to synthesise fused naphthyridines. Thus 3-aminobenzo[*f*]quinoline **108** was converted in this way into naphtho[2,1-*b*]-1,5-naphthyridine **109**.¹⁴¹ Similarly 2-aminobenzo[*h*]quinoline **110** was transformed into a mixture of naphthonaphthyridines **111** and **112** (yields 6.8% and 4.5%, respectively), and 3-aminobenzo[*g*]quinoline **113** gave rise to naphthonaphthyridine **114** (yield 4.2%). The naphthonaphthyridines **111** and **114** were also prepared from hydrogenated benzoquinolines **115** and **116**. Intermediates **117** and **118** were dehydrogenated by treatment with dichlorodicyanoquinone and palladium supported on carbon, respectively. In this case, the overall yields of products were substantially higher.¹⁴²



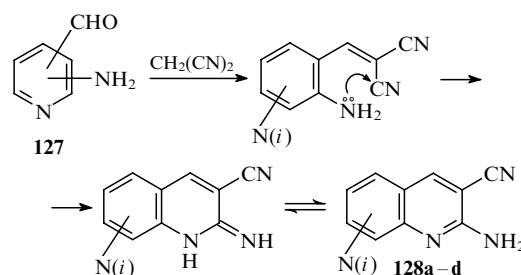
A modified Skraup method, namely, the reaction of 4-aminoisoquinoline **119** with methyl vinyl ketone in the presence of As_2O_5 and concentrated sulfuric acid, was used to prepare 4-methylbenzo[c]-1,5-naphthyridine **120** in 36% yield.¹⁴³ A similar reaction of 3-aminoquinoline **121** with crotonaldehyde or methyl vinyl ketone results in 2-methyl- (**122**) or 4-methyl-benzo[*f*]-1,7-naphthyridine **123**. Oxidation of the compounds **120**, **122** and **123** on treatment with SeO_2 in dioxane yields aldehydes **124**–**126**.



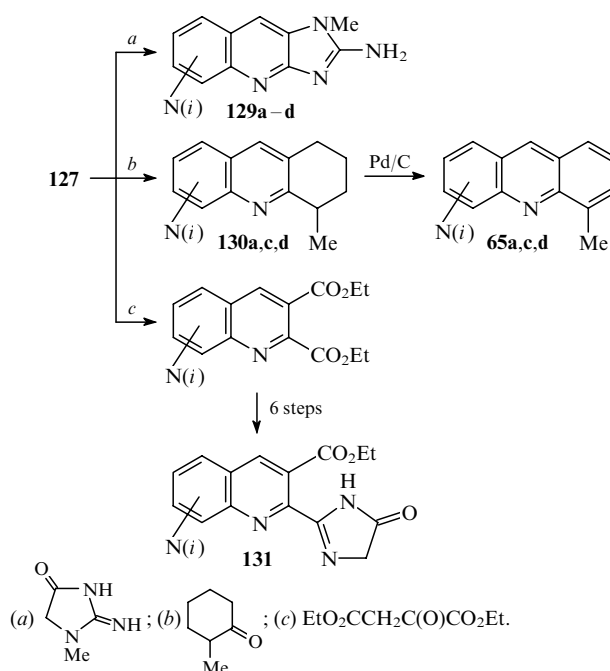
(a) $\text{CH}_2=\text{CHCOMe}$; (b) $\text{MeCH}=\text{CHCHO}$.

2. The Friedlander reaction in the synthesis of naphthyridines

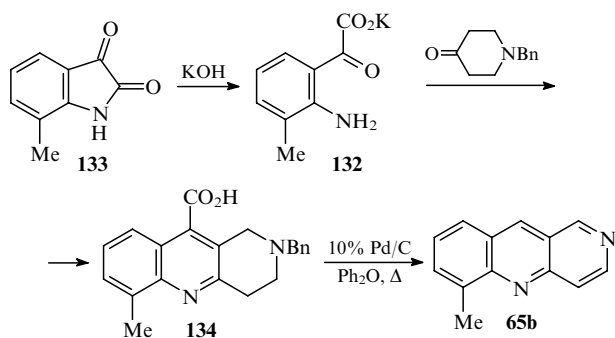
The condensation of vicinal aminopyridinecarbaldehydes **127** with malononitrile in ethanol in the presence of a base (according to the Knoevenagel reaction pattern) furnished 2-amino-3-cyano- $\text{N}(1),\text{N}(i)$ -naphthyridines **128a–d**; some of them were found to be effective diuretics.^{144, 145} The condensation of the aldehydes **127** with creatinine in ethylene glycol affords imidazo[4,5-*b*]- $\text{N}(1),\text{N}(i)$ -naphthyridines **129a–d**.¹⁴⁶ The reaction of the compounds **127** with 2-methylcyclohexanone in Bu^tOH in the presence of Bu^tOK (1.5 h, refluxing) followed by dehydrogenation of the products **130a,c,d** thus formed (refluxing with Pd/C in Ph_2O) gives rise to benzo[*b*]- $\text{N}(1),\text{N}(i)$ -naphthyridines **65a,c,d**. Using the Friedlander reaction, naphthyridines **131** have been synthesised; they are active components of herbicide formulations.^{147, 148} Benzo[*b*]-1,6-naphthyridine **65b** has been prepared by condensation of the amino acid salt **132** (obtained from 7-methylisatin **133**)



i = 5 (a), 6 (b), 7 (c), 8 (d).

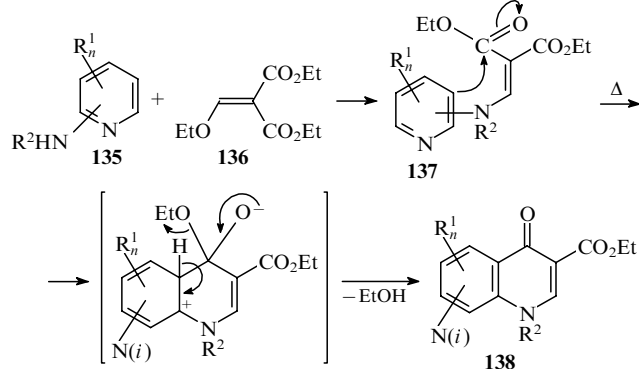


with *N*-benzylpiperidone (KOH, 0.5 h, < 40 °C; refluxing, 20 h) followed by dehydrogenation of the reaction product **134**.^{117–119}



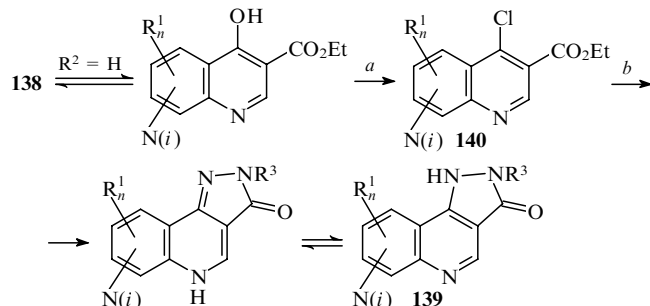
3. Condensation of aminopyridines with diethyl ethoxymethylidenemalonate

As in the previous cases, the use of condensation of aminopyridines with diethyl ethoxymethylidenemalonate for the synthesis of naphthyridines attracts attention because it provides the possibility of synthesising diverse naphthyridines exhibiting a broad range of biological activities. Thus the condensation of substituted aminopyridines **135** with diethyl ethoxymethylidenemalonate **136** and subsequent cyclisation on refluxing of the resulting diesters of *N*-(pyridyl)aminomethylidenemalononic acids **137** gives derivatives of naphthyridinecarboxylic acids **138**, possessing antibacterial activity or serving as intermediates in the synthesis of compounds with this type of activity.^{130, 149–161}

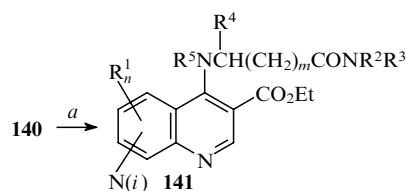


$n = 1, 2$; $R^1 = \text{Me, EtO, EtS, F, 4-pyridyl}$; $R^2 = \text{H, cyclopropyl}$.

Naphthyridines **138** ($R^2 = \text{H}$) without substituents at nitro- gen have served as the starting compounds *en route* to pyrazolo[3,4-*c*]naphthyridines **139**, which act as modulators of benzodiazepine receptors and possess sedative and antispasmodic activities.^{162–164} The reactions of chloronaphthyridines **140** with amino acid amides afford compounds **141**, which possess anxiolytic, anticonvulsive, sedative and hypnotic activities, antimicrobial and analgesic properties; they are capable of reducing blood pressure and are used as pharmaceuticals.^{165–167}

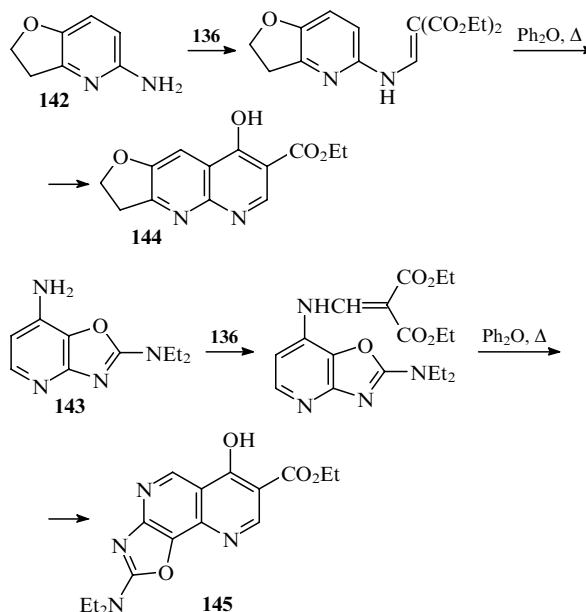


$n = 1, 2$; $R^1 = \text{Me, MeO}$; $R^2 = \text{Ph, pyridyl, quinolyl, isoquinolyl, pyrimidyl, thiazolyl}$; (a) $(\text{COCl})_2$, MeCN, DMF, from -30 to 20 °C; (b) $R^3\text{NHNH}_2$, xylene, Δ .



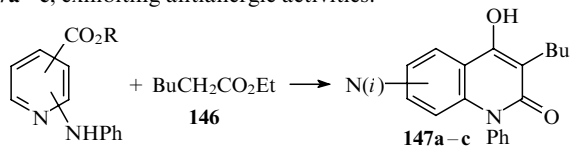
(a) $R^2R^3\text{NC(O)(CH}_2)_m\text{CH(R}^4\text{)NHR}^5$; $n = 1, 2$; $m = 0-2$; $R^1 = \text{Hal, Alk, AlkO, NO}_2, \text{CF}_3$; $R^2, R^3 = \text{H, Alk, Ph, Bn}$; $R^2-R^3 = (\text{CH}_2)_x$ ($x = 4-8$); $R^4 = \text{H, Alk, Bn}$; $R^5 = \text{H, Alk}$.

The condensation of diethyl ethoxymethylidenemalonate **136** with 5-amino-2,3-dihydrofuro[3,2-*b*]pyridine **142**¹⁵⁴ or 7-amino-oxazolo[4,5-*b*]pyridine **143**¹⁶⁸ results in annulated naphthyridines **144** and **145**. 2,3-Dihydrofuro[3,2-*b*]-1,8-naphthyridine **144** shows antibacterial activity.¹⁵⁴



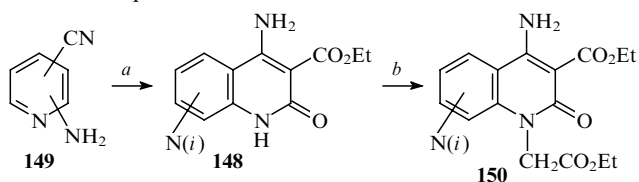
4. Condensation of aminopyridinecarboxylic acids and their derivatives with compounds containing an active methylene group

The condensation of vicinal aminopyridinecarboxylic acids or esters with ethyl hexanoate **146** in the presence of Bu^tOK under a nitrogen atmosphere gave *N*(1),*N*(*i*)-naphthyridin-2(1*H*)-ones **147a–c**, exhibiting antiallergic activities.¹⁶⁹



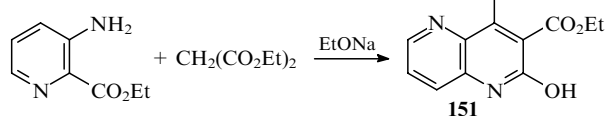
$R = \text{H, Me, Et}$; $i = 5$ (a), 7 (b), 8 (c).

Naphthyridones **148**, which are of interest as pharmacological preparations, have been synthesised by the reaction of vicinal aminopyridinecarbonitriles **149** with diethyl malonate. Alkylation of these products with ethyl monobromoacetate results in *N*-substituted compounds **150**.¹⁷⁰

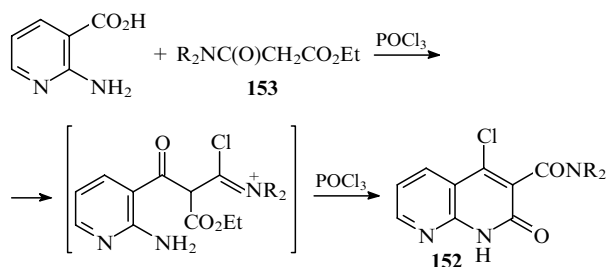


(a) $\text{CH}_2(\text{CO}_2\text{Et})_2$, EtONa; (b) $\text{BrCH}_2\text{CO}_2\text{Et}$, BuOH, K_2CO_3 ; $i = 5-8$.

When diethyl malonate is made to react with ethyl 3-aminopicolinate, substituted 1,5-naphthyridine **151** is formed; it is used in the synthesis of potential antimalarial remedies.¹⁷¹



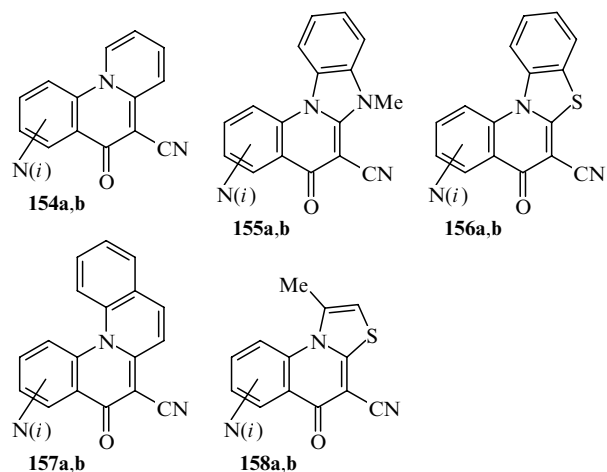
1,8-Naphthyridine-3-carboxamides **152** — starting compounds for the preparation of products with antihypertensive, antiphlogistic and antiaggressive activities — have been synthesised from 2-aminonicotinic acid and amido esters **153**. The synthesis includes the formation of the chloride and a salt of 2-aminonicotinic acid upon the reaction of **153** with POCl_3 . The subsequent reaction of these intermediates results in the C-acylated product, the condensation of which gives the compound **152**.¹⁷²



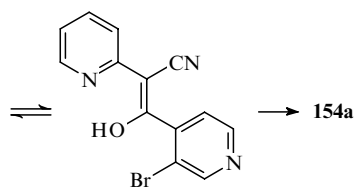
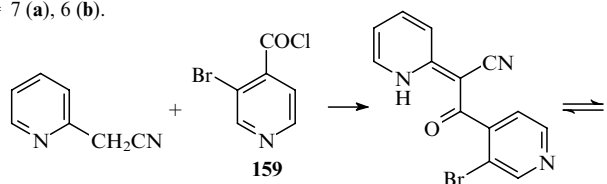
$\text{R}_2 = \text{Me}_2, \text{Et}_2, \text{Pr}_2^i, (\text{CH}_2)_5$.

5. Acylation of α -hetarylacetonitriles with halo-substituted nicotinic and isonicotinic acid chlorides

Fused azahetareno-1,7-naphthyridines **154a–158a**, containing a nitrogen atom in the bridgehead position, were obtained by the reaction of 3-bromoisonicotinic acid chloride **159** with 2-cyanomethyl derivatives of pyridine, 1-methylbenzimidazole, benzo-1,3-thiazole, quinoline or 4-methyl-1,3-thiazole followed by cyclisation of the resulting C-acylated derivatives on heating to the melting point or on refluxing in *N*-methyl-2-pyrrolidone (as shown for compound **154a** taken as an example).¹⁷³

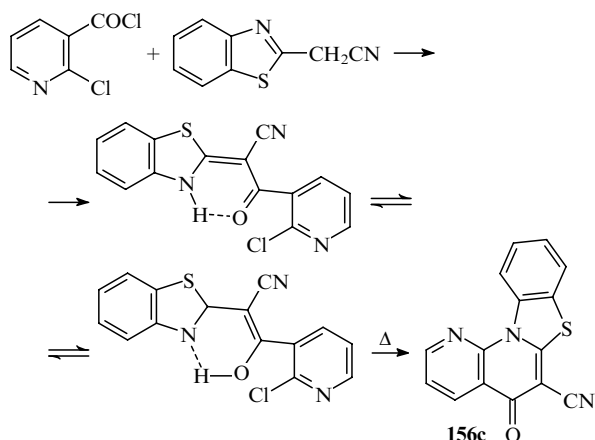


$i = 7$ (a), 6 (b).



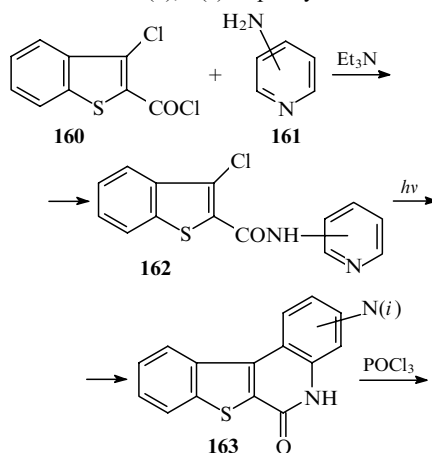
A similar reaction of 2-cyanomethyl derivatives of hetarenes with 4-chloronicotinoyl chloride yielded annelated azahetareno-1,6-naphthyridines **154b–158b**.¹⁷³ In this case, the intermediate C-acylated derivatives were not isolated because they easily cyclised to give **154b–158b**. 4,6-Dichloronicotinoyl chloride was used as the initial compound in this synthesis.¹⁷⁴

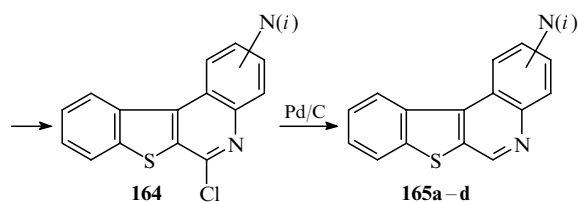
The product of interaction of 2-cyanomethylbenzo-1,3-thiazole with 2-chloronicotinoyl chloride cyclises on refluxing in DMF to give benzothiazolo[3,2-*a*]-1,8-naphthyridin-4-one derivative **156c**.¹⁷³



6. Photocyclisation of aminopyridines with chlorides of *ortho*-chlorinated hetarencarboxylic acids

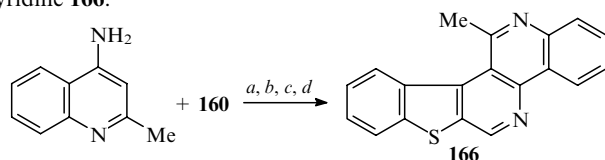
The reaction of 3-chlorobenzo[*b*]thiophene-2-carboxylic acid chloride **160** with 2-, 3- or 4-aminopyridine **161** in benzene in the presence of triethylamine has resulted in the synthesis of amides **162**, which undergo photocyclisation (UV irradiation by a medium-pressure mercury lamp, 450 W), giving rise to naphthyridines **163**.¹⁷⁵ Deoxygenation of these products on treatment with POCl_3 followed by dechlorination of compounds **164** results in [1]benzothieno-*N*(1),*N*(*i*)-naphthyridines **165a–d**.





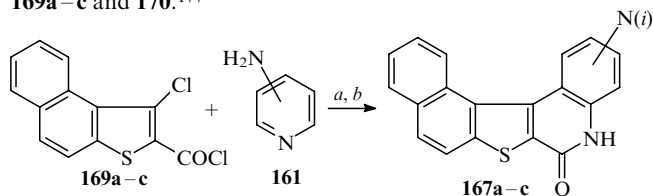
$i = 5$ (a), 6 (b), 7 (c), 8 (d).

Similarly, the reaction of chloride **160** with 4-amino-2-methylquinoline gave 1-methylbenzo[*h*][1]benzothieno[2,3-*c*]-1,6-naphthyridine **166**.¹⁷⁶

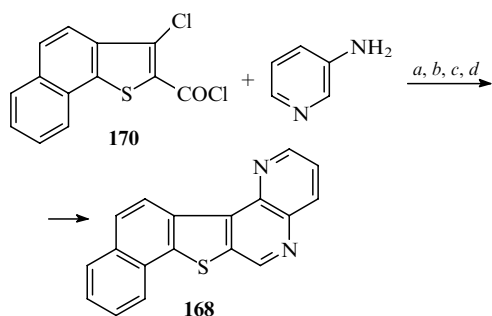


(a) Et₃N; (b) *hν*; (c) POCl₃; (d) Pd/C.

Photocyclisation is also one of the stages in the synthesis of naphtho[2,3-*b*]thieno-*N*(1),*N*(*i*)-naphthyridines **167a–c** and **168** from the chlorides of vicinal chloronaphtho[2,3-*b*]thiophenecarboxylic acids **169a–c** and **170**.¹⁷⁷



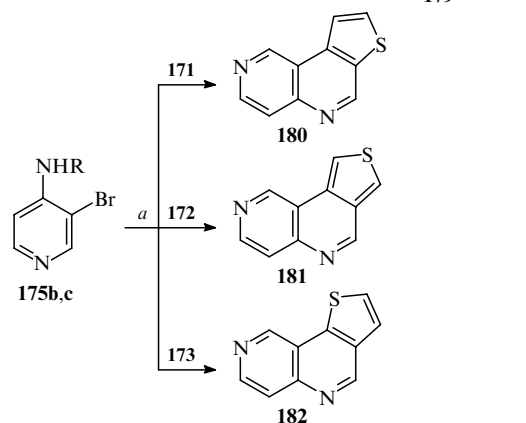
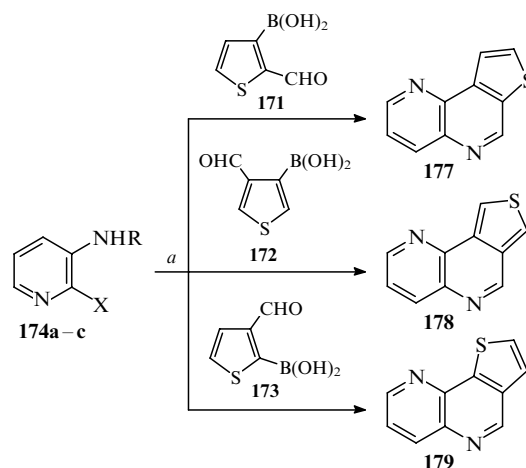
$i = 5$ (a), 6 (b), 7 (c).



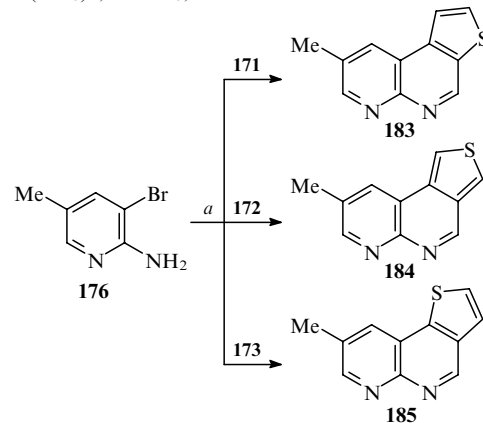
(a) PhH, Δ, 4 h; (b) *hν* (Hg lamp, 450 W), 1% MeOH in PhH, 3 h; (c) POCl₃, Δ, 4 h; (d) 10% Pd/C, KOH, MeOH–PhH (1 : 1), 20 °C, 24 h.

7. Synthesis of naphthyridines fused to a thiophene ring

A one-stage procedure has been proposed^{178–181} for the preparation of isomeric *N*(1),*N*(*i*)-naphthyridines; the procedure includes Pd(PPh₃)₄-catalysed cross-coupling of thiopheneboronic acids **171**, **172** or **173** containing an *ortho*-formyl group with *o*-amino-hetaryl halides **174–176**. The cross-coupling products cyclise spontaneously during the reaction to give thiophenonaphthyridines **177–185** with all possible types of ring fusion. The effects of the amount of the catalyst, the nature of the base and the reaction time on the yield of the naphthyridines **178** and **181** have been studied.¹⁸⁰

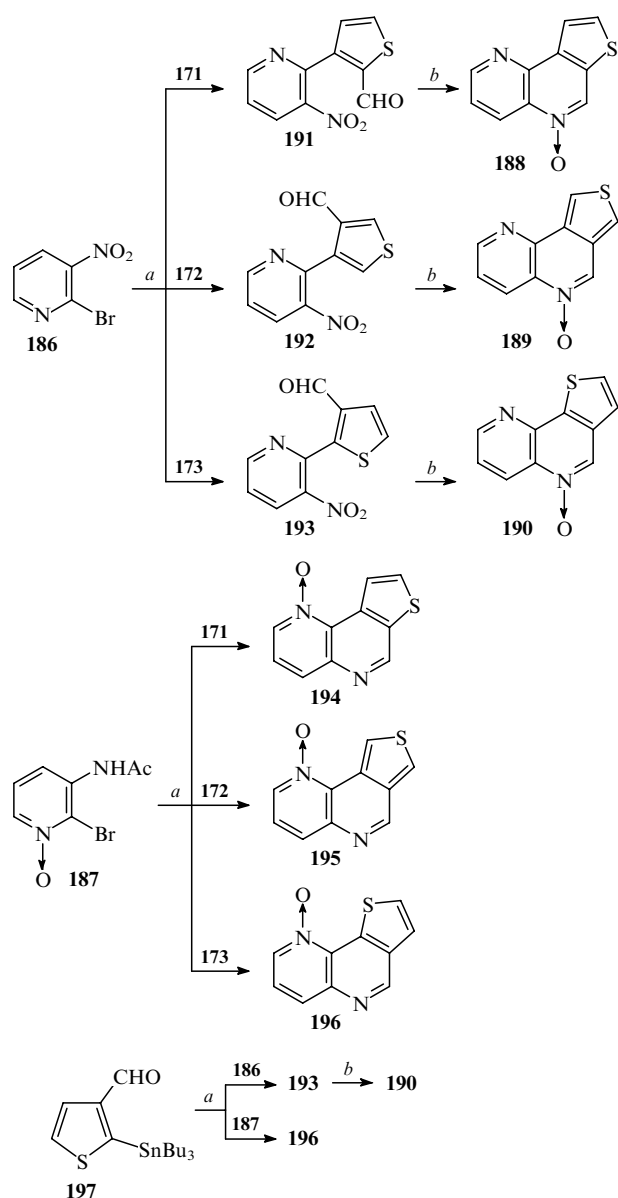


R = H: X = Cl (a), Br (b); R = Ac, X = Br (c);
(a) Pd(PPh₃)₄, Na₂CO₃, DME or DMF.



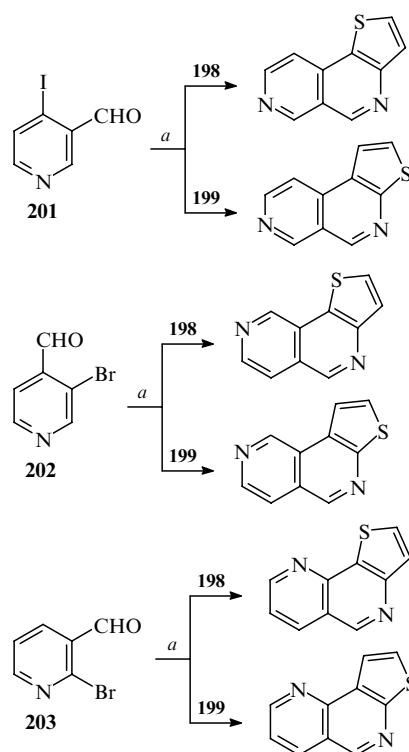
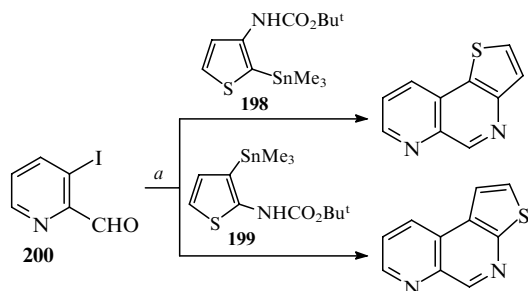
(a) Pd(PPh₃)₄, Na₂CO₃, DME or DMF.

When 2-bromo-3-nitropyridine **186** is employed in the cross-coupling with formylthiopheneboronic acids **171–173**, thieno-1,5-naphthyridine 5-oxides **188–190** are produced. However, in this case, cyclisation of the cross-coupling products **191–193** proceeds on treatment with FeSO₄ in NH₄OH. Isomeric thieno-1,5-naphthyridine 9-oxides **194–196** are formed upon cross-coupling of the formylboronic acids **171–173** with 3-acetyl-amino-2-bromopyridine oxide **187**. 2-Tributylstannyl-3-formylthiophene **197** can be used in the cross-coupling with aryl halides **186** and **187** instead of arylboronic acids. A mixture of *N*-oxide isomers **190** and **196** is also formed upon oxidation of thienonaphthyridine **179** with *m*-chloroperbenzoic acid.¹⁸¹



(a) Pd(0), Na₂CO₃, DME or DMF; (b) FeSO₄, NH₄OH.

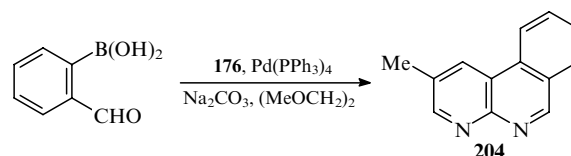
The reaction of vicinal trimethylstannyl derivatives of *tert*-butoxycarbonylaminothiophenes **198** and **199** with halo-substituted pyridinecarbaldehydes **200**–**203** in the presence of PdCl₂, CuO and bis(diphenylphosphino)butane results in fused thienonaphthyridines of all the possible types.¹⁸²



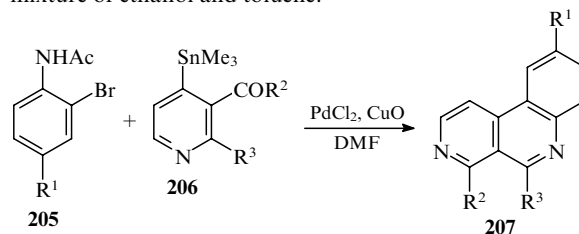
(a) PdCl₂, CuO, Ph₂P(CH₂)₄PPh₂.

The photoelectron spectra of all the thienonaphthyridine isomers have been analysed using semiempirical methods for the calculation of the ionisation energies of molecular orbitals.^{183, 184}

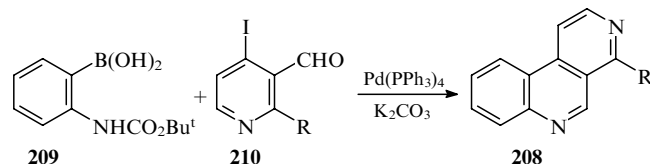
Cross-coupling catalysed by zerovalent palladium complexes has been employed to obtain other annelated naphthyridines. Thus the reaction of bromoaminopyridine **176** with 2-formylphenylboronic acid provided 9-methylbenzo[*c*]-1,8-naphthyridine **204**.¹⁷⁸



Cross-coupling of *o*-bromoacetanilides **205** with trimethylstannylpyridyl ketones **206** in the presence of PdCl₂ and CuO in DMF affords benzo[*c*]-2,7-naphthyridines **207**.¹⁸⁵ Benzo[*c*]-2,7-naphthyridines **208** were prepared by refluxing 2-*tert*-butoxycarbonylaminothiophenylboronic acid **209** with substituted iodonicotin-aldehydes **210** in the presence of Pd(PPh₃)₄ and K₂CO₃ in a mixture of ethanol and toluene.¹⁸⁶



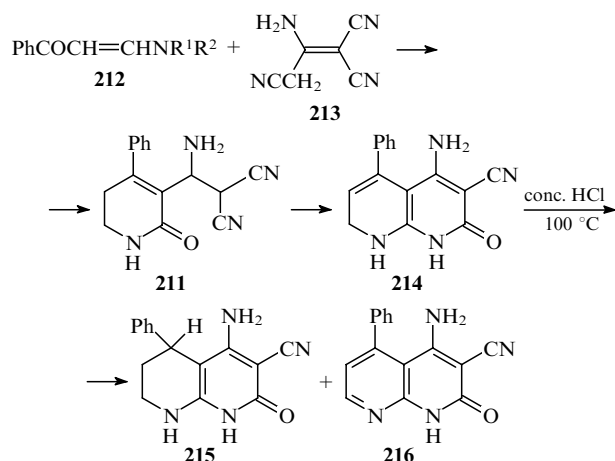
R¹ = H, Me, OMe; R² = H, Me; R³ = H, OMe.



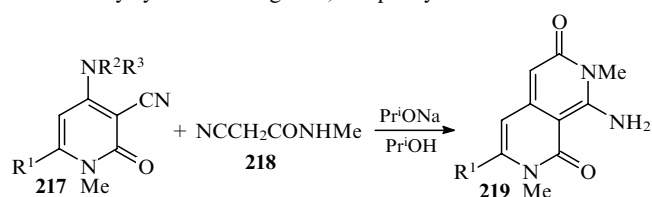
R = F, Cl, CONPr₂.

8. β -Enaminocarbonyl compounds in the synthesis of naphthyridines

β -Enaminocarbonyl compounds have long been used successfully in the synthesis of isomeric naphthyridines. Thus pyridone **211**, prepared by the reaction of β -enamino ketone **212** with 4,4-dicyano-3-aminobut-2-enitrile **213**, cyclises to give substituted 1,2,7,8-tetrahydro-1,8-naphthyridin-2-one **214**. On treatment with concentrated hydrochloric acid at 100 °C, compound **214** undergoes disproportionation giving rise to a mixture of hexahydro (**215**) and dihydro derivatives of 1,8-naphthyridin-2-ones **216**.^{187, 188}

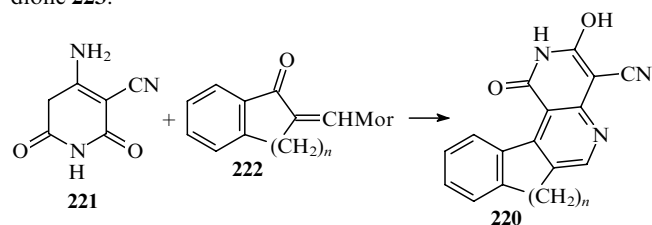


The reaction of 4-dialkylaminopyridones **217**, containing a β -enaminoamide fragment, with *N*-methylcyanoacetamide (**218**) is accompanied by replacement of the endocyclic amino group followed by cyclisation to give 2,7-naphthyridine **219**.¹⁸⁹

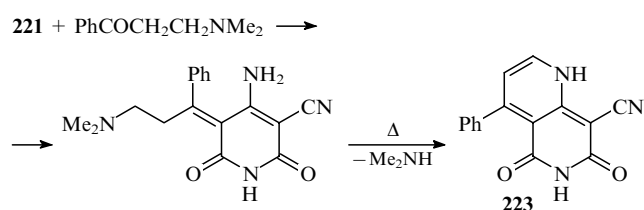


$\text{R}^1 = \text{Ph}, 4\text{-ClC}_6\text{H}_4, 4\text{-MeOC}_6\text{H}_4$; $\text{R}^2 = \text{Et}, \text{Ph}, \text{CH}_2\text{Ph}, \text{CH}_2\text{CH}(\text{OEt})_2$; $\text{R}^3 = \text{H}, \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$.

One approach to the construction of fused 1,6-naphthyridines **220** includes the reaction of 4-amino-2,6-dioxo-1,2,5,6-tetrahydro-3-pyridinecarbonitrile **221** with cyclic β -enamino ketones **222**. The pyridinedione **221** reacts with 3-dimethylamino-1-phenylpropan-1-one to give 1,5,6,7-tetrahydro-1,6-naphthyridine-5,7-dione **223**.^{190–192}

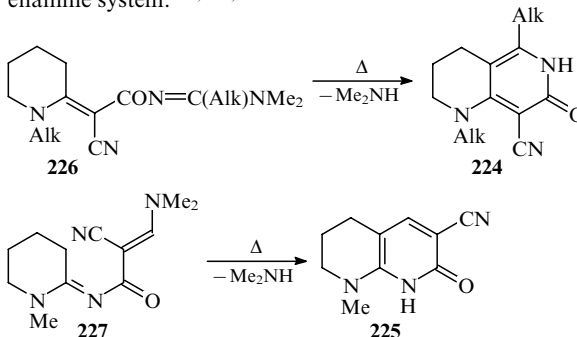


$n = 1–3$.



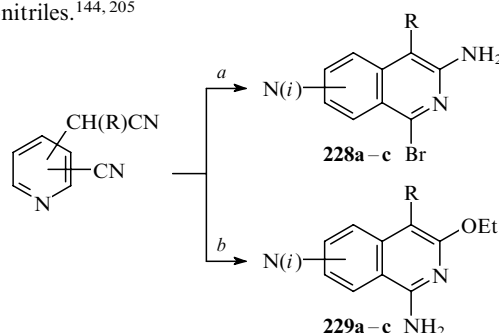
Enamino amides **226** and **227**, containing a β -enaminocarbonyl fragment, are promising starting compounds in the synthesis of hydrogenated naphthyridines **224** and **225**.^{193–204}

Study of the kinetics of these reactions demonstrated that the rate of cyclisation of the compounds **226** is much higher than that for the amidine **227**, due to the more pronounced delocalisation of the positive charge in the amidine system compared to the enamine system.^{195, 203, 204}

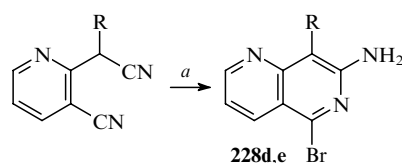


9. Cyclisation of 1,5-dinitriles and 1,5-amino(amido)nitriles of the pyridine series

Acid hydrolysis of 3- or 4-cyanopyridylacetoneitriles or their reaction with sodium ethoxide affords isomeric amino derivatives of naphthyridines **228a–c** and **229a–c**. The 1,6-naphthyridines **228d,e** have been prepared by hydrolysis of 2-cyanomethylnicotinonitriles.^{144, 205}

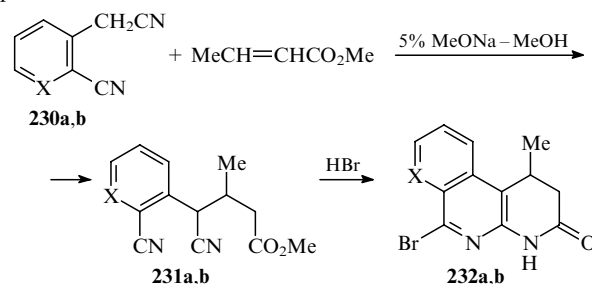


$\text{R} = \text{H}$: $i = 6, 7$; $\text{R} = \text{Me}$, $i = 6$; (a) HBr ; (b) EtONa .



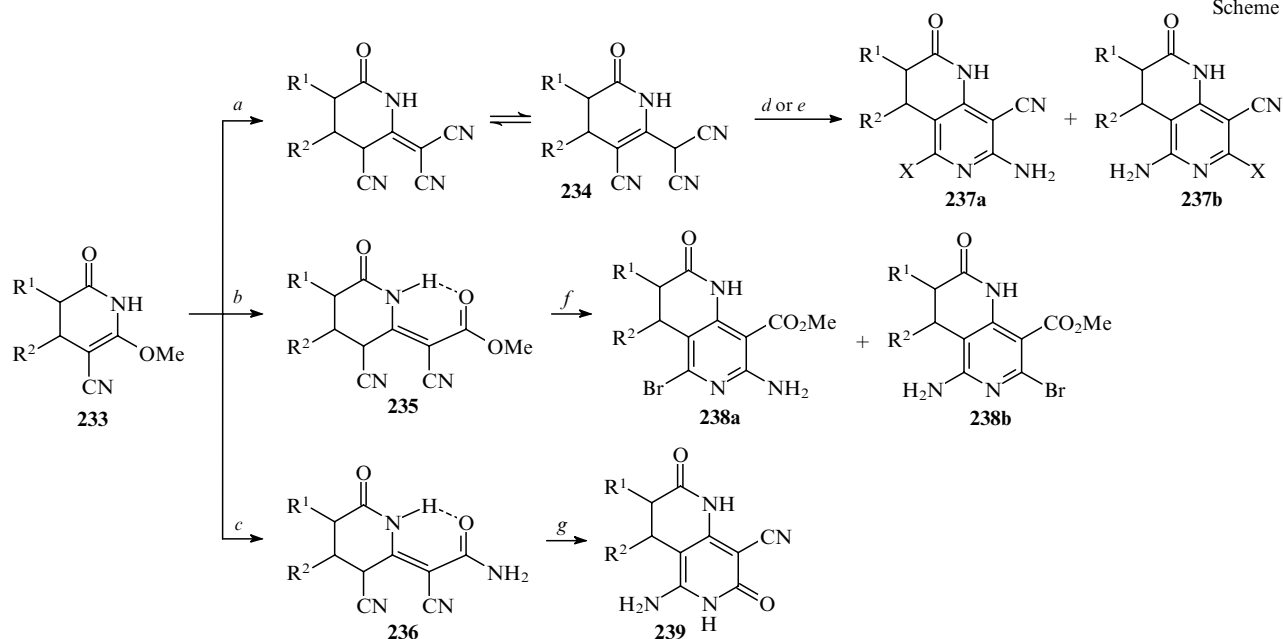
$\text{R} = \text{H}, 4\text{-FC}_6\text{H}_4$; (a) 30% HBr – AcOH .

2-Cyanophenyl- (**230a**) or 2-cyano-3-pyridylacetoneitriles **230b** react with methyl crotonate to give adducts **231a,b**. Subsequent acid-catalysed cyclisation of compounds **231a,b** gives rise to the corresponding pyrido- and benzo[*c*]-1,8-naphthyridines **232a,b**—potential means for treating heart weakness, stenocardia and hypertension.^{206, 207}



$\text{X} = \text{CH}$ (a), N (b).

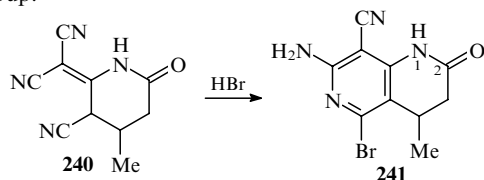
Scheme 4



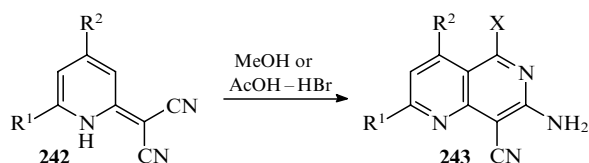
$\text{R}^1, \text{R}^2 = \text{H, Me, Ph}$; (a) $\text{CH}_2(\text{CN})_2$; (b) $\text{NCCH}_2\text{CO}_2\text{Me}$; (c) $\text{NCCH}_2\text{CONH}_2$; (d) HX , $\text{X} = \text{Cl, Br}$; (e) MeONa, MeOH , $\text{X} = \text{OMe}$; (f) HBr ; (g) OH^- , H_2O or RO^- , ROH .

The methoxy group in 5-cyano-6-methoxy-3,4-dihydro-2(1H)-pyridones **233** is replaced by malononitrile, methyl cyanoacetate or cyanoacetamide. The intermediates **234**–**236** cyclise in acid or basic media to give 3,4-dihydro-1,6-naphthyridine-2(1H)-ones **237**–**239** (Scheme 4).^{208, 209}

Cyclisation of piperidine **240** yields 1,6-naphthyridine monohydrate **241**. An X-ray diffraction study showed that the $\text{C}(2)–\text{N}(1)$ bond (1.362 Å) is longer than these bonds in other cyclic amides due to less efficient conjugation with the carbonyl group.²¹⁰

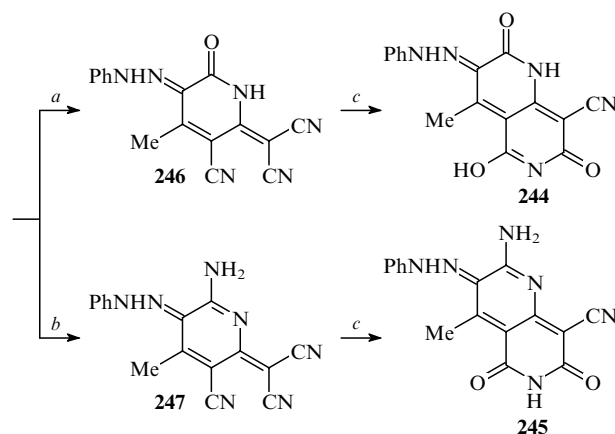
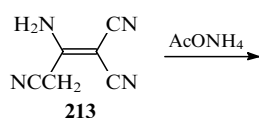


Dinitriles **242** have been used to perform regioselective synthesis of 7-amino-8-cyano-1,6-naphthyridines **243**.^{144, 211, 212}



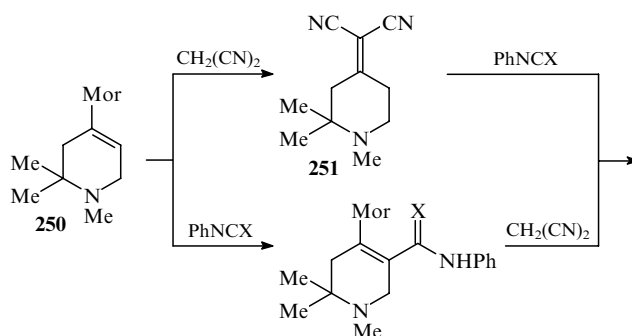
$\text{R}^1, \text{R}^2 = \text{Me, Et}$; $\text{X} = \text{Br, OMe}$.

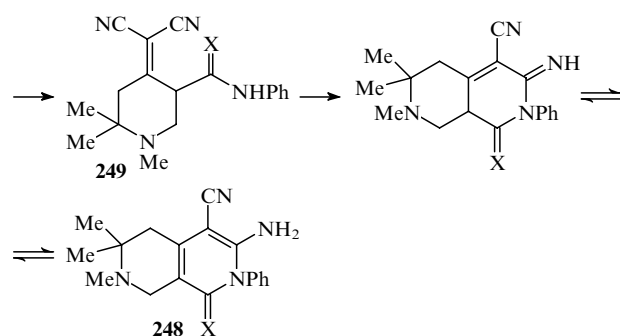
Naphthyridinediones **244** and **245** have been synthesised using reactions of 3-amino-4,4-dicyanobut-2-enenitrile (**213**) with α -diketone monophenylhydrazones. Cyclisation of intermediate dinitriles **246** and **247** was performed on treatment with a mixture of AcOH and HCl .²¹³



(a) $\text{PhNHN}=\text{C}(\text{Ac})\text{CO}_2\text{Et}$; (b) $\text{PhNHN}=\text{C}(\text{Ac})\text{CN}$; (c) AcOH, HCl .

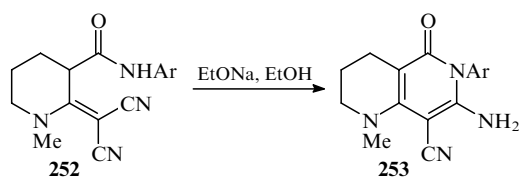
Enamino nitriles of 2,7-naphthyridinone(or -thione) **248** have been synthesised by cyclisation of amido(or thioamido) nitriles **249**, which are prepared from enamine **250** or substituted malononitrile **251**.^{214, 215}





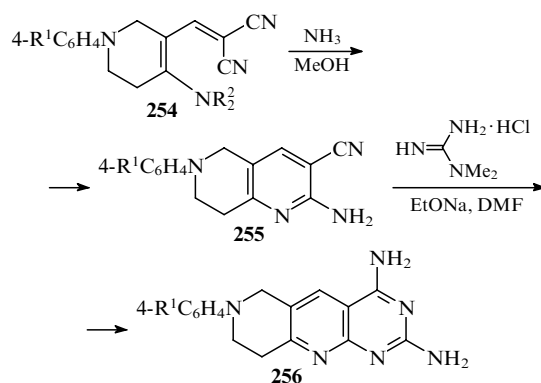
X = O, S.

On treatment with sodium ethoxide in ethanol, 1-methyl-2-dicyanomethylidenepiperidine-3-carbanilides **252** cyclise to give partially hydrogenated 1,6-naphthyridin-5(6*H*)-ones **253**.²¹⁶



Ar = Ph, 4-ClC₆H₄, 3-MeC₆H₄.

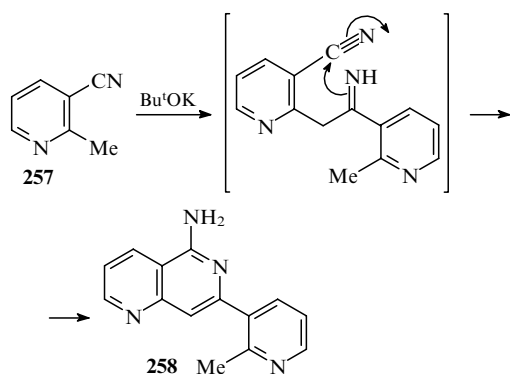
Ammonolysis of enamines **254**, obtained from 1-aryl-3-(2,2-dicyanovinyl)-4-piperidones affords 2-amino-6-aryl-3-cyano-5,6,7,8-tetrahydro-1,6-naphthyridines **255**, employed in the synthesis of pteridines **256**.²¹¹



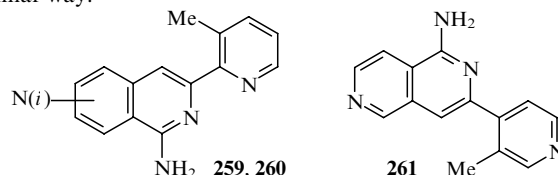
R¹ = Me, Et; R₂² = (CH₂)₄.

10. Thorpe dimerisation of cyanopicolines

Dimerisation of 2-methylnicotinonitrile (**257**) induced by potassium *tert*-butoxide and including intramolecular addition of the imine to the nitrile at the cyclisation stage gives rise to 5-amino-7-(2-methyl-3-pyridyl)-1,6-naphthyridine (**258**).¹³⁰



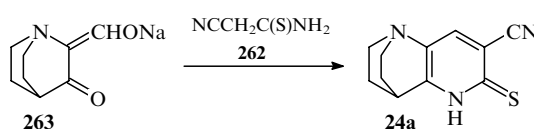
8-Amino-1,7-, 1-amino-2,6- and 1-amino-2,7-naphthyridines **259–261**, possessing efficient bactericidal and fungicidal activities, were prepared from the corresponding cyanopicolines in a similar way.¹⁴⁴



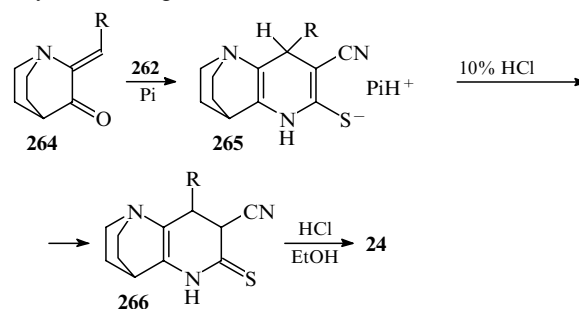
i = 6, 7.

11. Condensation of piperidones with cyanoacet(or thioacet)amides

The condensation of cyanothioacetamide **262** with the sodium salt of 2-formyl-3-quinuclidone **263** in ethanol in the presence of AcOH has resulted in the synthesis of 1,5-naphthyridine-2(1*H*)-thione **24a**.¹⁰⁶

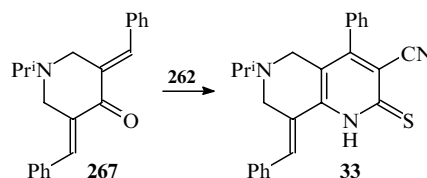


Cyanothioacetamide **262** condenses with 2-arylmethylidene-3-oxoquinuclidines **264** in the presence of piperidine to yield relatively stable salts **265**; in an acid medium, these products are converted into 3,4-dihydro-1,5-naphthyridinethiones **266**. Upon refluxing in an HCl–EtOH mixture, the compounds **266** are transformed into naphthyridinethiones **24**, which are also formed directly on refluxing the salts **265** in an ethanolic solution of HCl.

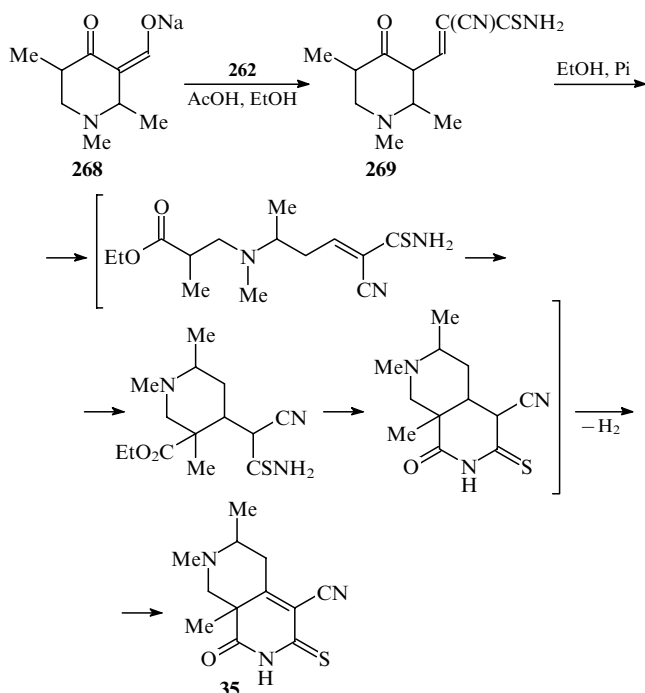


R = H, Ph, 4-FC₆H₄; Pi is piperidine.

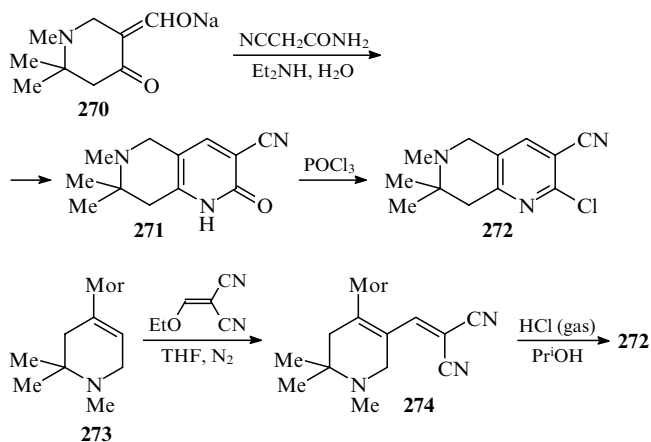
The partially hydrogenated 1,6-naphthyridinethione **33** has been synthesised by the reaction of 3,5-bis(phenylmethylidene)-1-isopropyl-4-piperidone **267** and the amide **262**.¹⁰⁷



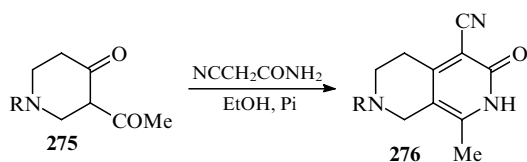
The reaction of the salt **268** with the amide **262** in ethanol in the presence of AcOH follows the Knoevenagel reaction route and affords adduct **269**, which recycles when refluxed in ethanol in the presence of a catalytic amount of piperidine, giving rise to the 2,7-naphthyridine **35**. The compound **35** is the product of a cascade type reaction comprising acidic cleavage according to Claisen, the Michael intramolecular addition, the interaction between the thioamide and ester groups and dehydrogenation.¹¹⁰



The cyclocondensation of piperidone **270** with cyanoacetamide in the presence of diethylamine gives 1,6-naphthyridinone **271**, which reacts with POCl₃ to give chloro derivative **272**.²¹⁷ The compound **272** was also prepared by condensation of enamine **273** with ethoxymethylidenemalononitrile followed by cyclisation of intermediate **274**.²¹⁷



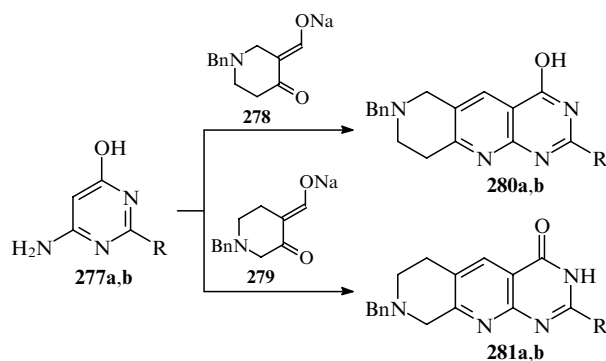
Refluxing of 1,3-dicarbonyl compounds **275** with cyanoacetamide in ethanol in the presence of piperidine gives 2,7-naphthyridine derivatives **276**, used as components of formulations for treatment of diseases of blood circulation organs.²¹⁸



R = H, Alk, Ph, Ac, Bn, 4-pyridyl.

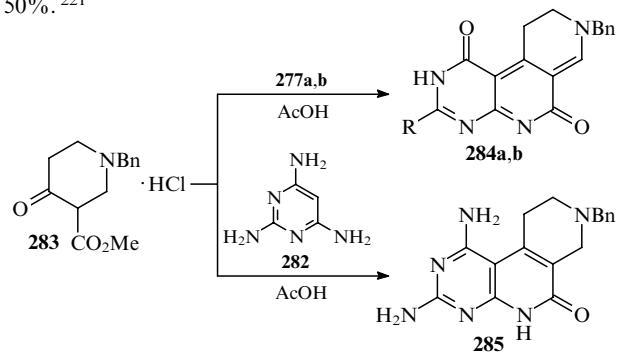
12. Cyclocondensation of piperidones with aminopyrimidines

When aminopyrimidines **277** are heated (100 °C, 3 h) with the salts of isomeric hydroxymethylidenepiperidones **278** and **279** in 85% orthophosphoric acid, substituted tetrahydropyrimido[4,5-*b*]-1,6- (**280a,b**)²¹⁹ and -1,7-naphthyridines **281a,b** are formed;²²⁰ they are potential antitumour remedies.

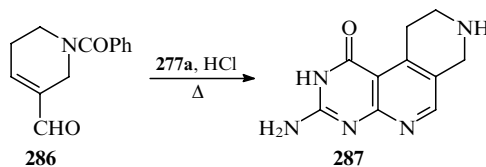


R = NH₂ (a), OH (b).

Refluxing of aminopyrimidines **277a,b** and **282** with methyl 1-benzyl-4-oxopiperidine-3-carboxylate hydrochloride **283** in glacial acetic acid provided the synthesis of pyrimido[4,5-*c*]-2,7-naphthyridin-6-ones **284a,b** and **285**. The compounds **284b** and **285** present in concentrations of 10⁻⁵ and 2 × 10⁻⁶ mol litre⁻¹, respectively, inhibit *in vitro* the growth of malignant leukemia cells by 50%.²²¹

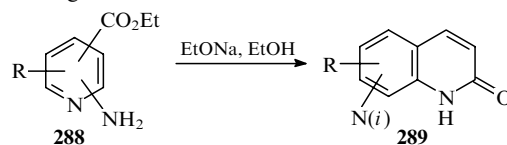


A similar condensation of the aminopyridine **277a** with hydrogenated 3-formylpyridine **286** in the presence of HCl in ethanol results in tetrahydropyrimido[4,5-*c*]-2,7-naphthyridine **287** mixed with its 7-benzoyl derivative.^{219, 222}

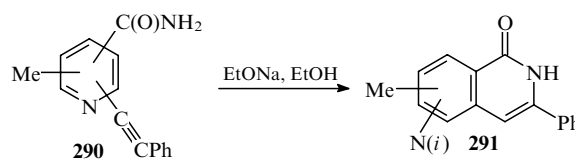


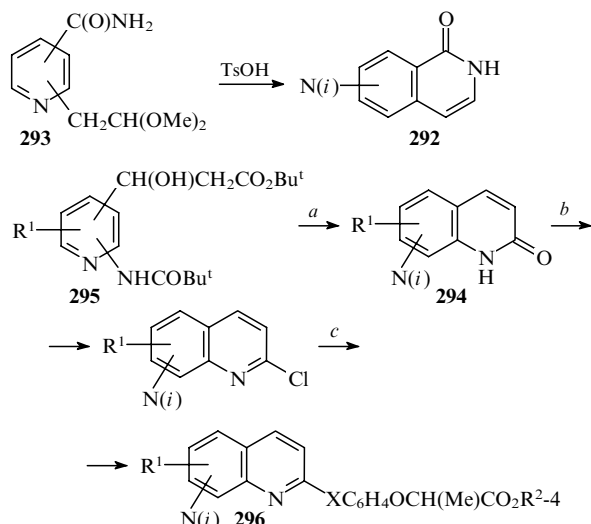
13. Other general methods for the synthesis of naphthyridines

Below we present the syntheses of naphthyridines starting from pyridine derivatives containing an amino (or protected amino) group and a carbonyl group or its synthetic equivalent in vicinal positions. Cyclisation is accomplished by treatment with basic or acidic reagents.

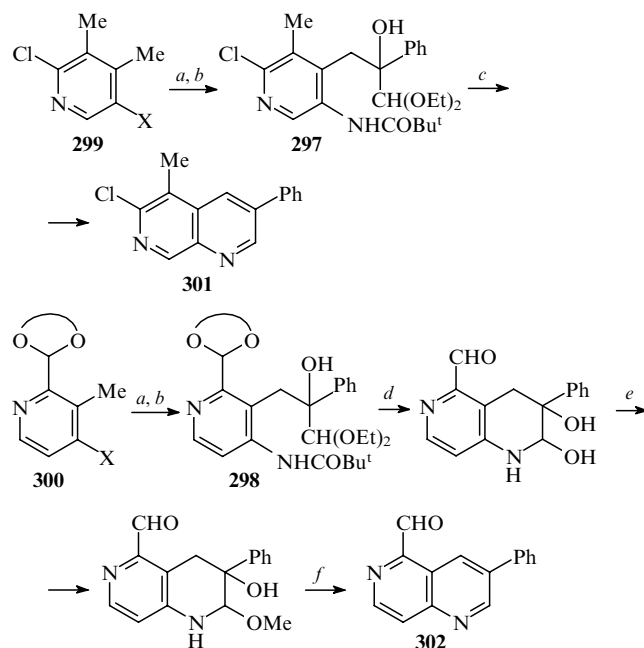


R = H, Me; *i* = 5–8.





$i = 6-8$; $R^1 = \text{H, Me, Cl}$; $R^2 = \text{Alk}$; $X = \text{O, S}$; (a) 3 M HCl; (b) POCl_3 , Δ ; (c) $4\text{-HXC}_6\text{H}_4\text{OCH}(\text{Me})\text{CO}_2\text{R}^2$, K_2CO_3 or NaH , DMSO.

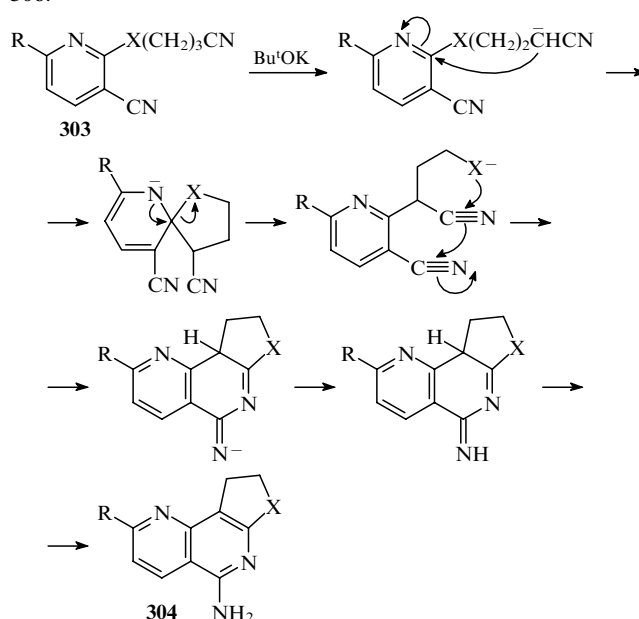


(a) Bu^nLi ; (b) $(\text{EtO})_2\text{CHCOPh}$; (c) HCl; (d) H_2SO_4 ; (e) MeOH, H_3PO_4 ; (f) diazabicycloundecene, dioxane, Δ .

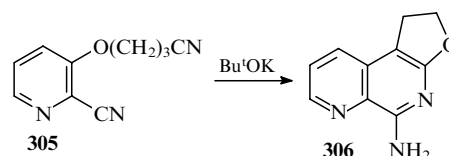
Cyclisation of ethyl aminopyridineacrylates **288** in ethanol in the presence of sodium ethoxide has served as a route to $\text{N}(1),\text{N}(i)$ -naphthyridin-2(1H)-ones **289**.²²³ Cyclisation of ethynylpyridinecarboxamides **290** under similar conditions yields 1,6-, 1,7-, 2,6- and 2,7-naphthyridones **291**.²²⁴ Naphthyridones **292** were prepared by refluxing vicinal (2,2-dimethoxyethyl)pyridinecarboxamides **293** with toluene-*p*-sulfonic acid in benzene.²²⁴ $\text{N}(1),\text{N}(i)$ -Naphthyridin-2(1H)-ones **294**, prepared by refluxing vicinal 2-*tert*-butoxycarbonyl-1-hydroxyaminopyridines **295** in dioxane in the presence of 3 M HCl, have been used to obtain naphthyridine derivatives **296**, which possess herbicidal and fungicidal properties and are efficient for the protection of cotton, soy-bean and sugar-cane crops.^{225, 226} Intramolecular cyclisation of substituted *tert*-butoxycarbonylaminopyridines **297** and **298**, synthesised from compounds **299** and **300** via a two-stage procedure, gives 1,7- (**301**) and 1,6-naphthyridines **302**.²²⁷

2-(3-Cyanopropyl-oxy or -thio)pyridine-3-carbonitriles **303** undergo an intramolecular nucleophilic rearrangement, similar to the Smiles rearrangement, being thus converted into fused 1,6-naphthyridines **304**.²²⁸⁻²³⁰ A similar cyclisation of 2-pyridinecar-

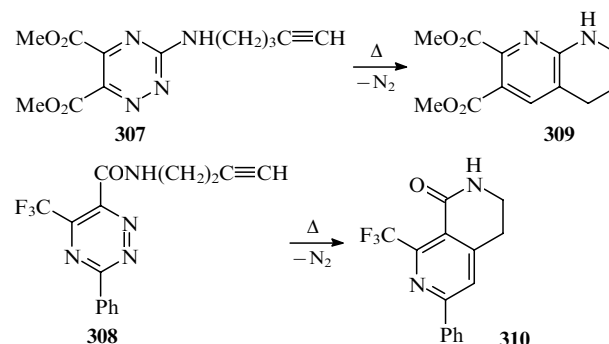
bonitrile **305** gives rise to dihydrofuro[3,2-*f*]-1,7-naphthyridine **306**.²³¹



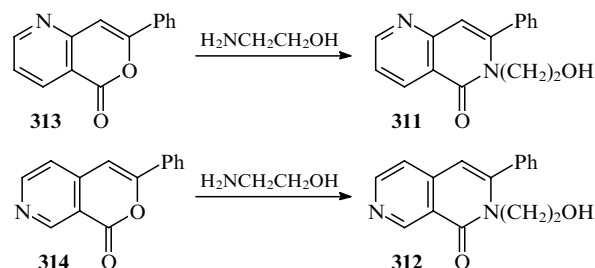
$X = \text{S}$, $R = \text{H}$; $X = \text{O}$, $R = \text{Me}$.



Substituted 1,2,4-triazines decompose on thermolysis with nitrogen evolution. Thermolysis of compounds **307** and **308**, having an ethynyl substituent in the side chain, yields substituted naphthyridines **309**²³² and **310**.²³³

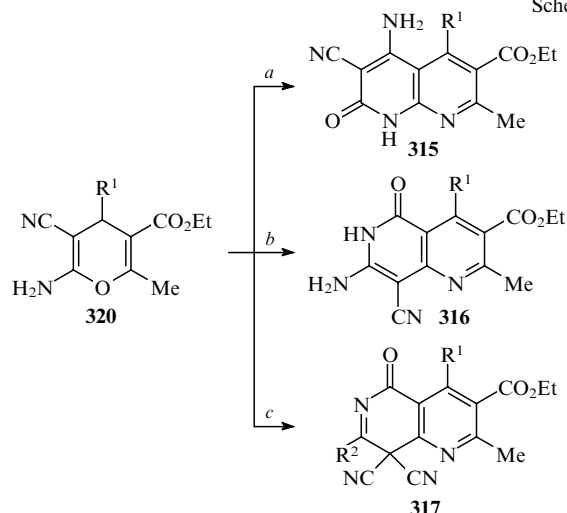


N-Hydroxyethyl-substituted 1,6- (**311**) and 2,7-naphthyridones **312** were prepared by refluxing the pyranopyridine isomers **313** and **314** with ethanolamine.²³⁴



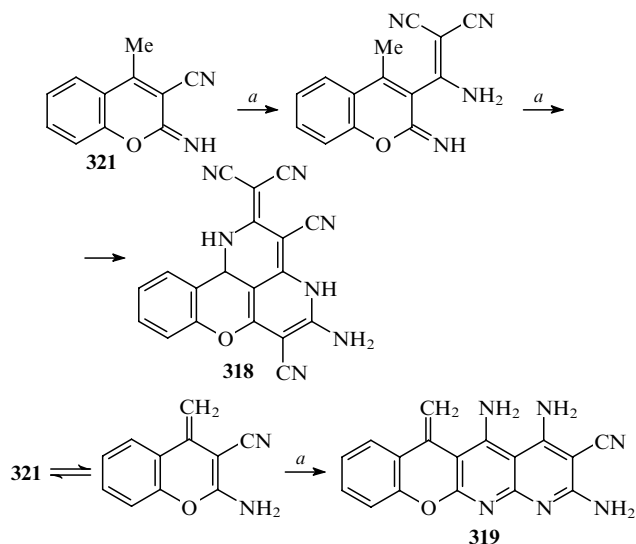
The synthetic routes to 1,8- (**315**) and 1,6-naphthyridones **316** and **317** and annelated systems **318** and **319** make use of the reactions of pyrans **320** and **321** with malononitrile or its derivatives. The reactions are carried out in ethanol in the presence of piperidine (Scheme 5).²³⁵⁻²³⁷

Scheme 5



$R^1 = 2\text{-ClC}_6\text{H}_4, 4\text{-ClC}_6\text{H}_4, 4\text{-MeC}_6\text{H}_4;$

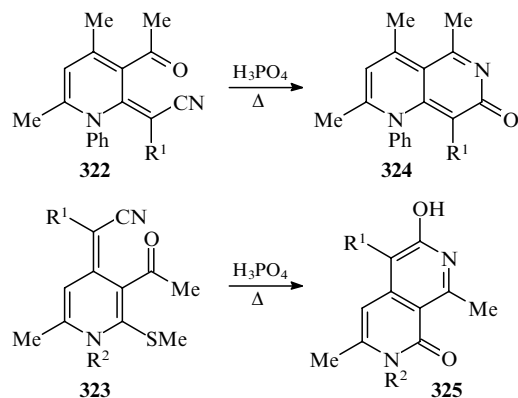
(a) $\text{NCCH}_2\text{CONH}_2$; (b) $\text{CH}_2(\text{CN})_2$; (c) $\text{R}^2\text{CH}=\text{C}(\text{CN})_2$; $\text{R}^2 = \text{Alk, Ar.}$



(a) $\text{NCCH}_2\text{CONH}_2$.

3-Acetyl-2-cyanomethylidenepyridine **322** and 3-acetyl-4-cyanomethylidenepyridine **323** cyclise on heating (130 °C, 30–45 min) in 85% orthophosphoric acid to give 1,6- (**324**) and 2,7-naphthyridinone derivatives **325** (Scheme 6).²³⁸

Scheme 6



$R^1 = \text{CN, CO}_2\text{Et}; R^2 = \text{Ph, 4-MeOC}_6\text{H}_4.$

V. Conclusion

The data surveyed here demonstrate that general and facile methods for the synthesis of diverse substituted naphthyridines are now available. Various naphthyridines can be synthesised

under the same conditions using similar equipment. Various types of biological activity exhibited by many naphthyridine derivatives together with the ease of their preparation make these products attractive objects for the search for new highly effective medicinal preparations, which can be done using combinatorial synthesis.

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Sulfamides in the synthesis of heterocyclic compounds

G A Gazieva, A N Kravchenko, O V Lebedev

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Abstract. A comparative analysis of the structures and physicochemical properties of sulfamides and ureas has been performed. New procedures for the synthesis of heterocyclic compounds containing the sulfamide fragment are surveyed and the properties of the resulting compounds are described. The bibliography includes 112 references.

I. Introduction

The chemistry of sulfamides has received sufficient attention in the literature. The synthesis, physicochemical properties and reactions of these compounds have been considered many times in reviews which were partially or completely devoted to sulfamides.^{1–13} However, the latest review¹³ was published more than 10 years ago. During the last decade, abundant experimental data have accumulated, which call for further generalisation.

Sulfamides attract permanent interest because acyclic and cyclic products containing sulfamide fragments exhibit a broad spectrum of physiological activities. Thus sulfamoylamidines possess antiulcerous¹⁴ and diuretic¹⁵ activities, 4-phenyl-1,2,5-thiadiazolidin-3-one 1,1-dioxide exhibits antispasmodic activity,¹⁶ 5-alkyl-2-phosphinyloxymethyl-1,2,5-thiadiazolidin-3-one 1,1-dioxides are proposed for the treatment of rheumatoid arthritis,¹⁷ and 1,2,5-thiadiazolidine 1,1-dioxides containing an indole substituent at position 2 are used for the treatment of migraine.^{18,19} 5-Alkyl-2-fluoromethyl-1,2,5-thiadiazolidin-3-one 1,1-dioxides inhibit enzymes, *viz.*, human leucocyte elastase and cathepsin G.²⁰ 6,7-Dihydro-5*H*-cyclopenta[*c*]- and 5,6,7,8-tetrahydrobenzo[*c*]-2,1,3-thiadiazine 2,2-dioxides act as myorelaxants,²¹ and 3,5-dioxo-1,2,6-thiadiazine 1,1-dioxides are used as antiinflammatory agents.²² Aryl-substituted seven- and eight-membered cyclic sulfamides inhibit HIV-1 protease.^{23,24} Many sulfamides possess antibacterial properties.^{25,26}

Sulfamides are also used in photography,²⁷ they are components of fungicide²⁸ and insecticide²⁹ mixtures and are employed as detergents.³⁰ 3,5-Dioxo- and 3,5-diimino-1,2,6-thiadiazine 1,1-dioxides are used for the preparation of azo dyes.³¹ 3-Amino-1,2,6-thiadiazine 1,1-dioxides exhibit fungistatic activities.³²

S,S-Dioxides of benzothiadiazine, thiadiazine, and thiatriazine as well as some acyclic sulfamides can serve as herbicides.^{33–35}

In the 1980s, a new class of chiral oxidising agents based on sulfamides was found. These are 2-sulfamoyloxaziridines which exhibit high enantioselectivity (40%–91%) in asymmetric oxidation of sulfides to sulfoxides.^{36–38}

It is believed^{1,7,14,39–42} that the increased interest in sulfamide derivatives stems from the fact that these compounds are structurally similar to ureas. In this connection, we thought that it was worthwhile performing a comparative analysis of the structures and physicochemical properties of sulfamide and urea. However, the major aim of the present review is to systematise procedures for the synthesis of heterocyclic compounds based on sulfamide. Wherever possible, a comparative analysis of the properties of cyclic sulfamides and of the corresponding cyclic ureas was carried out.

II. Structure and physicochemical properties of sulfamide

Whereas the electronic structure of the carbonyl group has been studied comprehensively and described in detail, the data on the electronic structure of the sulfonyl group are ambiguous. The character of the S–O bond remains unclear, and the question of whether this bond is purely polar, semipolar, covalent or ‘intermediate’ is still open.

The question about the nature of the sulfonyl groups is closely related to the question about the participation of the *d* orbitals of the sulfur atom in bonding with other elements and to the question of whether the sulfur atom can exhibit ‘hypervalence’ thus violating the Lewis octet rule.⁴³

Quantum-chemical calculations with the 3-21G* and 6-31G* basis sets (*i.e.*, taking into account the contribution of the *d* orbitals) for a series of model compounds containing the SO and SO₂ groups demonstrated that the contribution of the *d* orbitals to the formation of the S–O bond is insignificant.^{44,45} Thus Reed and von Ragué Schleyer⁴⁴ concluded that the character of the S–O bond is determined primarily by the partially ionic σ bond and the π – σ^* ‘negative hyperconjugation’. However, studies of the electronic structures of sulfamides and heterocyclic compounds containing the SO₂ group by calculation methods demonstrated that p_π – d_π interaction with the participation of the *d* orbitals of the sulfur atom contributes to the formation of the multiple S–O bond.^{45–50} According to these calculations, the S–O bond has two components of the σ and π types, *viz.*, the σ bond between the corresponding atomic orbitals of the oxygen and sulfur atoms and the π bond between, on the one hand, three lone electron pairs of the oxygen atom polarised toward the sulfur

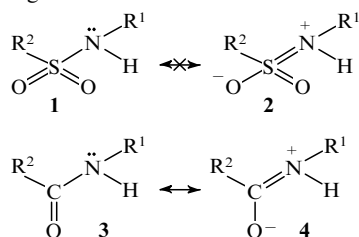
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atom, and, on the other hand, the p and d orbitals of the sulfur atom. However, the S–O bond is not, strictly speaking, a double bond because the π type of interaction is $p_\pi-d_\pi$ bonding with the participation of all three electron pairs of the oxygen atom. Nevertheless, as in Ref. 43, we shall arbitrarily denote these bonds as O=S=O. It should be remembered that these ‘double’ bonds differ substantially from true double bonds formed by elements of the second row (for example, from C=O bonds) and are characterised by a substantial contribution of the ionic state.^{43–50}

The specificity of the structure of the sulfo group is reflected in the spatial configuration of the atoms in the sulfamide molecule as well as in the electron density distribution. Recently, the crystal structure of sulfamide has been studied by X-ray and neutron diffraction analysis (Table 1).^{49, 51, 52} According to the results of these studies, the S and N atoms in the sulfamide molecule have tetrahedral and pyramidal bond configurations, respectively, whereas the nitrogen atom in amides and urea is characterised by sp^2 hybridisation and a planar bond configuration.⁵² The urea molecule is planar and symmetrical. The bond angles in this molecule differ little from 120°. This structure is consistent with the notion of conjugation between the π electrons of the C=O double bond and the lone electron pairs of the nitrogen atoms. This conjugation cannot occur in the sulfamide molecule because the sulfur atom does not possess unoccupied orbitals for participation in electron delocalisation. It has been demonstrated^{45, 47} that the d orbitals of the sulfur atom are not involved in bonding with the S and N atoms in sulfamides. It was also found that sulfonamides cannot adopt the limiting resonance structure 2 analogous to the structure 4 for carboxamides.⁵⁷



The electron-withdrawing effect of the SO₂ group is stronger than that of the carbonyl group, and hence the acidity of the amino groups in sulfamide is higher than that in urea. Thus the amino groups in urea exhibit a weakly basic character, whereas

Table 1. Comparative characteristics of the sulfamide and urea molecules.

Parameter	Sulfamide	Urea
Bond lengths / Å		
S–O	1.434	C–O 1.276
S–N	1.614	C–N 1.356
N–H	1.034	N–H 1.046
N–H'	1.038	N–H' 1.070
Bond angles / deg		
O–S–O'	118.0	O–C–N 120.9
O–S–N	106.2	N–C–N' 118.2
O'–S–N	107.0	C–N–H 122.5
N–S–N'	111.7	C–N–H' 120.5
H–N–H'	112.5	H–N–H' 117.0
Dihedral angle / deg	OSO/NSN 89.39	
Stretching vibrations / cm ^{–1}		
N–H	3210–3372	N–H 3342–3449
SO ₂	1315–1369, 1145–1155	C=O 1681
SN ₂	870–955	CN 1004, 1466

Note. The geometric parameters for the sulfamide molecule were taken from Refs 51 and 52, the parameters for the urea molecule were taken from Ref. 53, and the stretching vibration frequencies were published in Refs 53–56.

these groups in sulfamide are weakly acidic. Urea forms salts with acids⁵⁸ and sulfamide gives salts with heavy metals (for example, AgNHSO₂NHAg) and alkali metals.^{1, 12, 59} These data agree with the Taft induction constants σ_1 for the electron-withdrawing substituents in dioxane (σ'_1) and in weakly acidic solvents (σ''_1).⁶⁰

Group	σ'_1	σ''_1
CONH ₂	0.11	0.21 ± 0.02
SO ₂ NH ₂	0.38	0.46 ± 0.03

Therefore, sulfamide can be considered as an analogue of carbamide only bearing in mind that the N–SO₂ conjugation is actually not realised in sulfamide by virtue of electronic and steric factors and that, in addition, the NH bond in sulfamide is substantially more acidic, and, correspondingly, the nitrogen atom is less basic than those in urea.

The results of *ab initio* calculations^{45–50} of the geometry, dipole moments, atomic charges and bond orders in sulfamides and heterocyclic compounds containing the NSO₂N fragment agree well with the experimental data.

In the crystal, the sulfamide molecules, like the urea molecules, are linked together through strong hydrogen bonds,^{51, 52, 54, 58} which may be responsible for the rather high melting points of these compounds. In solutions of sulfamides, these hydrogen bonds are substantially weaker and are observed only in water, which is confirmed by the data from IR and Raman spectroscopy.⁵⁵

The ¹⁵N, ¹⁴N and ³³S NMR spectra of sulfamide have also been reported.^{61, 62}

III. Synthesis of heterocyclic compounds containing the sulfamide fragment

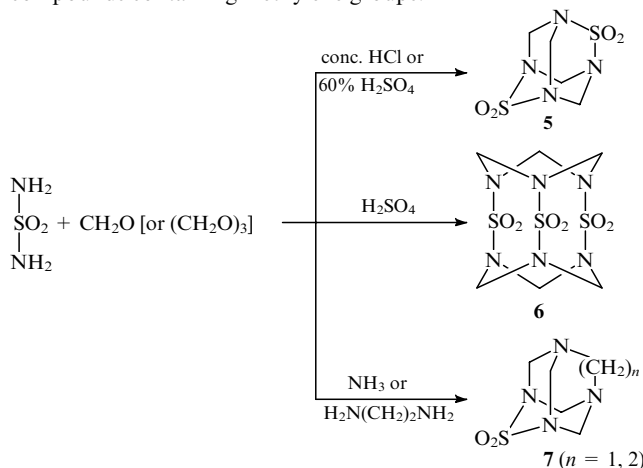
Since heterocyclic systems containing the NSO₂N fragment are highly diversified, we believe that it is more convenient to classify procedures for their synthesis according to the initial compounds, as in Ref. 12, rather than according to the resulting products, as in Ref. 13.

Sulfamide and urea are not as strong nucleophiles as ammonia or amines; nevertheless, they can also react with electrophilic reagents. Reactions of sulfamides with carbonyl compounds, diamines, dinitriles and other bifunctional reagents are considered in this Section.

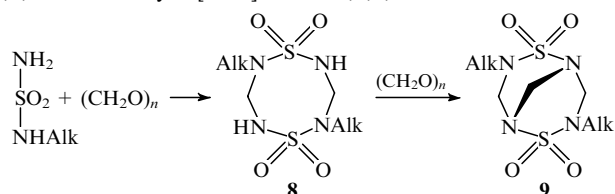
1. Reactions of sulfamides with carbonyl compounds

One of the most general procedures for the synthesis of heterocyclic compounds based on sulfamides involves their condensation with carbonyl compounds^{39, 63–72} or with their acetals.^{41, 42, 73}

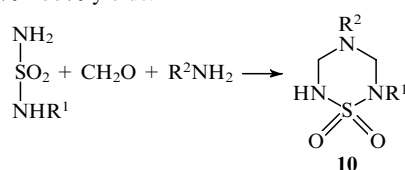
Formaldehyde,^{7, 12, 13, 63, 65} paraformaldehyde⁶⁴ and trioxane⁶³ are most commonly used in the synthesis of heterocyclic compounds containing methylene groups.



Reactions of alkylsulfamides with paraformaldehyde in trifluoroacetic acid occur through the intermediate formation of 1,5-dithia-2,4,6,8-tetraazocine 1,1,5,5-tetroxides **8** to yield 2,6-dithia-1,3,5,7-tetraazabicyclo[3.3.1]nonane 2,2,6,6-tetroxides **9**.⁶⁴



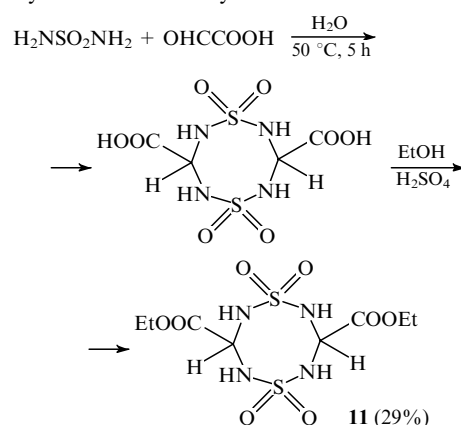
Condensation of sulfamides with formaldehyde and primary amines afforded tetrahydro-1,2,4,6-thiatriazine 1,1-dioxides **10** in 60%–86% yields.⁶⁵



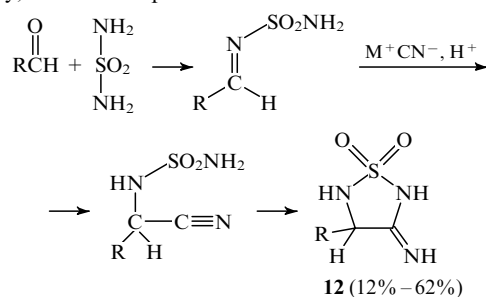
R¹ = H, OAlk, OAr; R² = Alk, Ar.

Ureas also react with formaldehyde to form a wide variety of products (both polymeric and heterocyclic) including compounds analogous to compounds **8** and **10**.^{7, 74, 75}

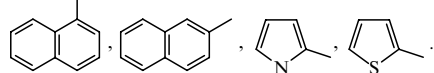
3,7-Bis(ethoxycarbonyl)perhydro-1,5-dithia-2,4,6,8-tetraazocine 1,1,5,5-tetroxide (**11**) was prepared from sulfamide and glyoxylic acid followed by esterification.⁶⁶



3-Imino-4-substituted 1,2,5-thiadiazolidine 1,1-dioxides (**12**) were formed upon boiling of solutions of aldehydes, sodium (or potassium) cyanide and sulfamide in aqueous ethanol.³⁹ Presumably, the reaction proceeds as follows:

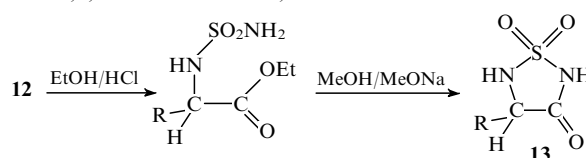


R = *n*-C₆H₁₃, PhCH₂CH₂, Ph, 4-MeOC₆H₄, 3,4,5-(MeO)₃C₆H₂,

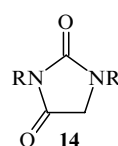


This reaction did not take place with paraformaldehyde, trioxane, acetone and acetophenone.

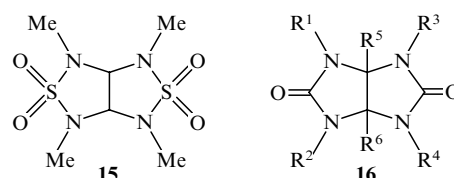
3-Oxo derivatives **13** are prepared from the corresponding 3-imino-1,2,5-thiadiazolidine 1,1-dioxides.



Unlike sulfamide derivatives **13**, 2,4-dioxoimidazolidines **14** are readily formed from ureas and α-dicarbonyl compounds in an acidic medium.^{7, 76}

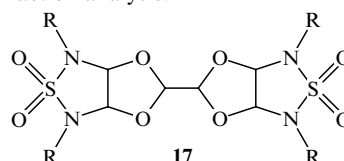


Over many years, the reactions of sulfamides with α- and β-dicarbonyl compounds have also been widely used in the synthesis of heterocyclic compounds.^{5, 12, 13, 67–71} Thus the reaction of *N,N'*-dimethylsulfamide with glyoxal in an acidic medium (pH 3–4) afforded the first representative of bis(sulfamides) of the bicyclooctane series, *viz.*, 2,4,6,8-tetramethyl-3,7-dithia-2,4,6,8-tetraazabicyclo[3.3.0]octane 3,3,7,7-tetroxide (**15**), (the yield was 23%).⁶⁷



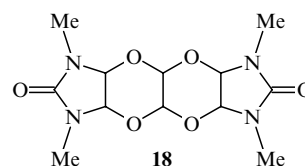
It should be noted that analogous bicyclic bisureas **16** have been prepared long ago from ureas and α-dicarbonyl compounds in 91% yield. Over the past century, tens of representatives of this class of compounds have been synthesised,^{7, 77} whereas sulfamide analogues have been previously unknown.

With the aim of increasing the yield of compound **15**, we performed the reactions of *N,N'*-dialkylsulfamides with glyoxal monohydrate in 36.7% hydrochloric acid. However, new heterocyclic compounds, *viz.*, 3,3'-bis(6,8-dialkyl-2,4-dioxo-7-thia-6,8-diazabicyclo[3.3.0]octane 7,7-dioxides) (**17**, the yields were 54%–85%), were obtained instead of the expected products **15**. The structures of the products **17** were confirmed by X-ray diffraction analysis.

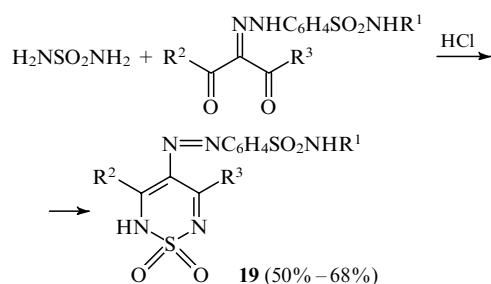


R = Me, Et, Pr, Bu.

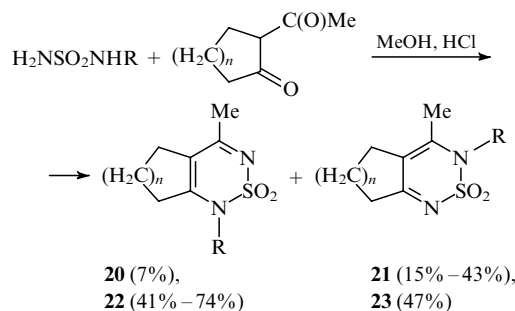
The reaction of *N,N'*-dimethylurea with glyoxal afforded another product, *viz.*, 4,6,12,14-tetramethyl-2,8,10,16-tetraoxa-4,6,12,14-tetraazatetracyclo-[7.7.0.0^{3,7}0^{11,15}]hexadecane-5,1-3-dione (**18**).⁷⁸



Reactions of sulfamide with β-diketones yielded various 1,2,6-thiadiazine 1,1-dioxide derivatives.^{70, 71}



$\text{R}^1 = \text{H}, \text{CH}_2\text{CONH}_2, \text{C}(\text{NH}_2)=\text{NH}, \text{Ar}; \text{R}^2 = \text{Me}, \text{Ph}; \text{R}^3 = \text{Me}, \text{Ph}.$

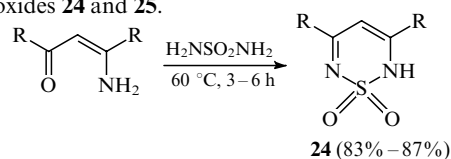


$\text{R} = \text{H}, \text{Me}; n = 1 \text{ (20, 21)}, 2 \text{ (22, 23)}.$

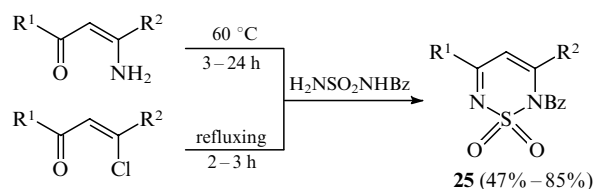
Reactions of sulfamide with symmetrical β -diketones afforded one type of products (**19**, $\text{R}^2 = \text{R}^3$); however, the reactions with unsymmetrically substituted β -diketones gave mixtures of tautomers (**20–23**, $\text{R} = \text{H}$). Moreover, the reactions of unsymmetrically substituted β -diketones with monosubstituted sulfamides afforded mixtures of regioisomers (**20–23**, $\text{R} = \text{Me}$).^{70–72}

The reactivity of β -diketones with respect to sulfamide depends on both the electronic and steric characteristics of the substituents in the diketones. Thus 3,5-diphenyl-2*H*-1,2,6-thiadiazine 1,1-dioxide and its 2-butyl derivative were prepared in 45% and 39% yields, respectively, whereas 3,5-di-*tert*-butyl-2*H*-1,2,6-thiadiazine 1,1-dioxide has not been synthesised yet.⁷²

It was demonstrated⁷² that the reactions of β -amino- and β -chloro- α,β -unsaturated ketones with sulfamide occurred regio-specifically under milder conditions than the reactions with the corresponding β -diketones. In anhydrous ethanol in the presence of HCl, these compounds gave a series of 2*H*-1,2,6-thiadiazine 1,1-dioxides **24** and **25**.

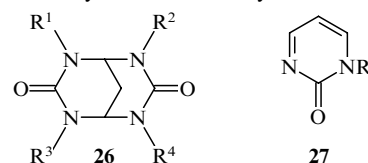


$\text{R} = \text{Me}, \text{Ph}, \text{Bu}^t.$

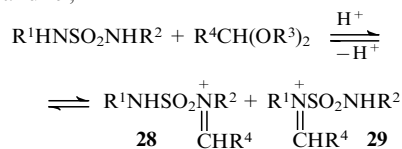


$\text{R}^1 = \text{Alk}, \text{Ar}; \text{R}^2 = \text{H}, \text{Me}.$

In the reactions of ureas with β -dicarbonyl compounds, bicyclic products **26** were formed more readily than 2-oxodihydropyrimidines **27**, whereas the reactions with β -chloro- α,β -unsaturated aldehydes afforded only derivatives **27**.^{7,79}



The use of acetals of carbonyl compounds instead of these compounds as such in the reactions with sulfamides resulted in the formation of six- and eight-membered *N,S*-containing heterocyclic compounds analogous to those described above along with new unexpected intramolecular α -sulfamidoalkylation products.^{41,42,73} Presumably,^{42,73} the mechanism of these reactions is analogous to the mechanism of α -ureidoalkylation.⁷ Reactions of sulfamides with acetals in an acidic medium afforded iminium ions **28** and **29**,



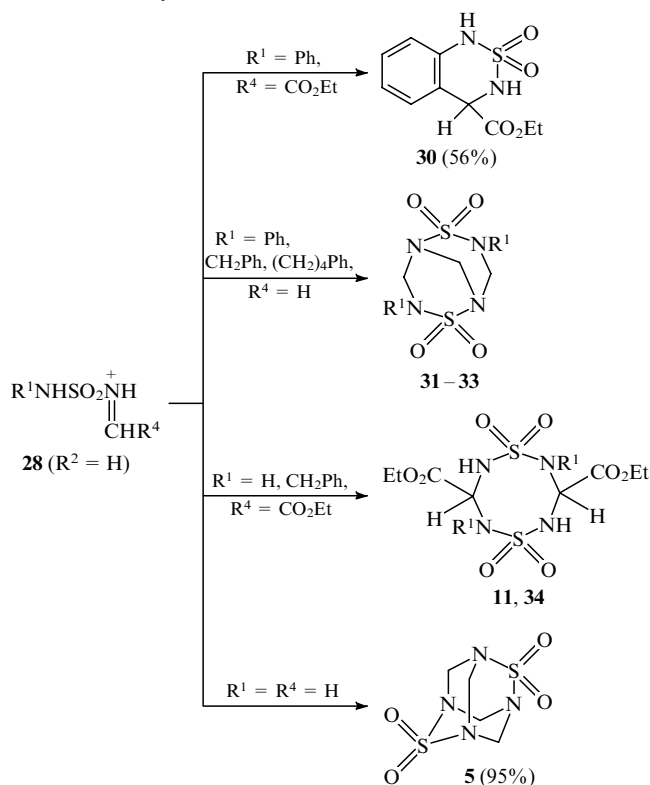
$\text{R}^1 = \text{H}; \text{R}^2 = \text{H}, (\text{CH}_2)_n\text{Ph}, \text{CH}_2\text{C}_6\text{H}_4\text{OMe-3};$

$\text{R}^1 = \text{R}^2 = (\text{CH}_2)_n\text{Ph} (n = 0-4);$

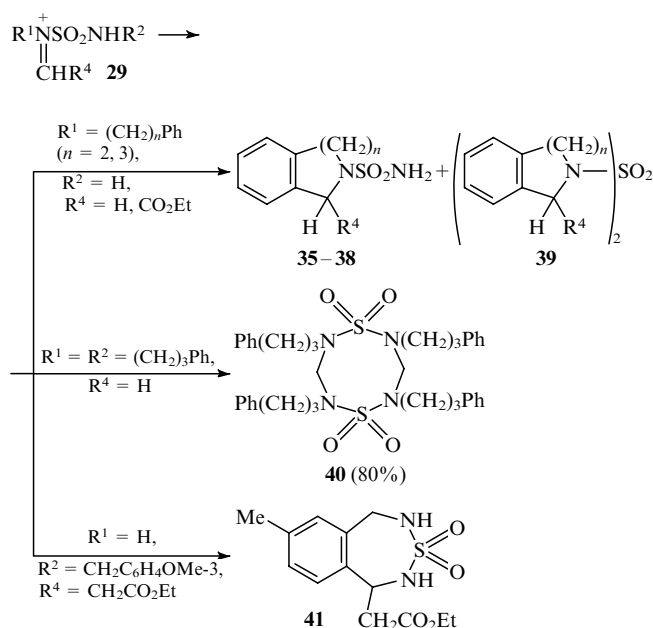
$\text{R}^3 = \text{Me}, \text{R}^4 = \text{H}; \text{R}^3 = \text{Et}; \text{R}^4 = \text{H}, \text{CO}_2\text{Et}, \text{CH}_2\text{CO}_2\text{Et};$

which underwent intramolecular or intermolecular α -sulfamidoalkylation depending on the nature of the substituent in the sulfamides and the reaction conditions.

In the case of α -sulfamidoalkylation of the aromatic rings in the iminium ions, annelation products **30**, **35–38** and **41** were formed. If the aromatic substituent in sulfamide is either remote from the generated iminium ion or absent, intermolecular dimerisation occurs to form eight-membered heterocyclic compounds **11**, **34** and **40**. Under certain conditions, these products can react with acetals to form compounds **5** and **31–33**. Symmetrical diarylsulfamides react with acetals $(\text{EtO})_2\text{CH}(\text{CH}_2)_m\text{COOEt}$ ($m = 0$ or 1) to form new sulfamide **39** as a result of intramolecular α -sulfamidoalkylation.

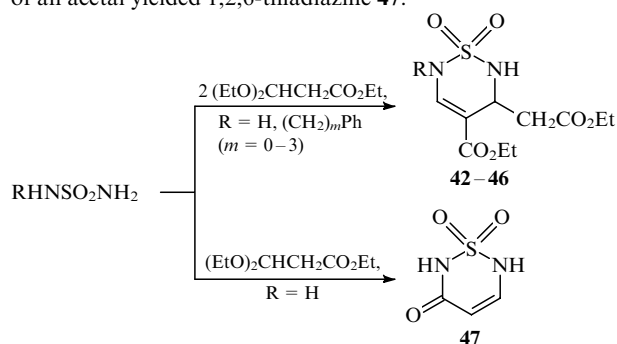


Compound	R^1	Yield (%)
31	Ph	46
32	CH_2Ph	72
33	$(\text{CH}_2)_4\text{Ph}$	56
11	H	75
34	CH_2Ph	74



Compound	<i>n</i>	R ⁴	Yield (%)
35	2	H	88
36	2	CO ₂ Et	80
37	3	H	85
38	3	CO ₂ Et	11
39	3	CO ₂ Et	68

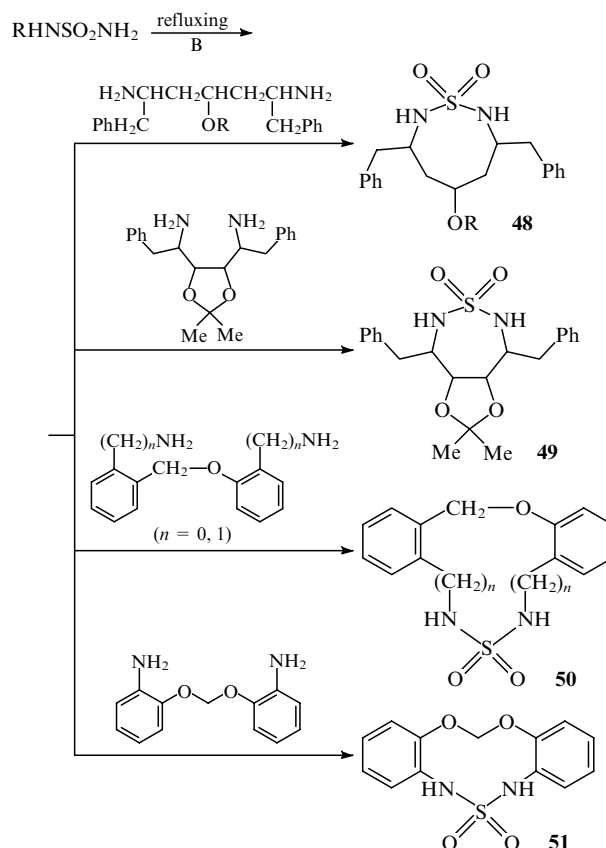
The reactions of unsubstituted sulfamide and arylsulfamides with two equivalents of an acetal in an acidic medium afforded 1,2,6-thiadiazines **42–46**, while the reaction with one equivalent of an acetal yielded 1,2,6-thiadiazine **47**.



Compound	R	Yield (%)
42	H	38
43	Ph	42
44	CH ₂ Ph	68
45	(CH ₂) ₂ Ph	37
46	(CH ₂) ₃ Ph	79

2. Reactions of sulfamides with diamines

An efficient procedure for the synthesis of heterocyclic compounds containing the sulfamide fragment involves condensation of sulfamide with diamines.^{12, 13, 23, 24, 80} This procedure allows one to prepare heterocyclic compounds with five, six or more atoms in the ring. Note that this procedure is the most convenient method for the synthesis of the latter compounds.



B is an organic base.

Heating of ureas with diamines is also used in the synthesis of heterocyclic compounds.⁸¹

3. Reactions of sulfamides with dinitriles

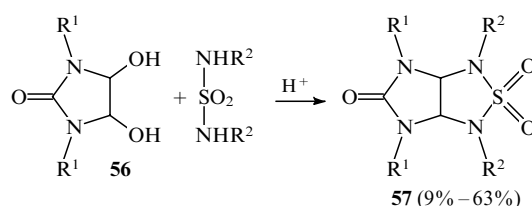
The reactions of sulfamides with dicyan and malonodinitriles find wide application.^{13, 82–86} Numerous examples of the preparation of diamino and diimino derivatives of 1,2,5-thiadiazole 1,1-dioxides and 1,2,6-thiadiazine 1,1-dioxides (**52–55**) are documented (Scheme 1).

Acid hydrolysis of compounds **52** and **54** afforded the corresponding 3-oxo derivatives.^{85, 86}

4. Condensation of sulfamides with diols and other bifunctional reagents

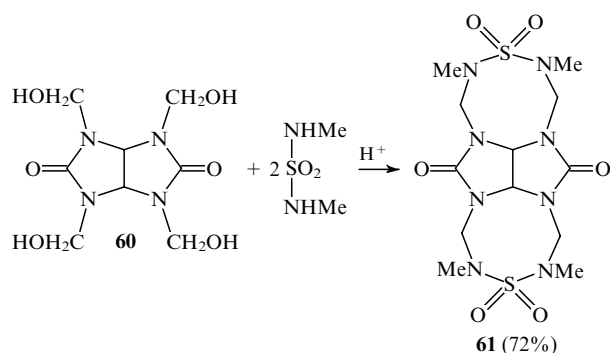
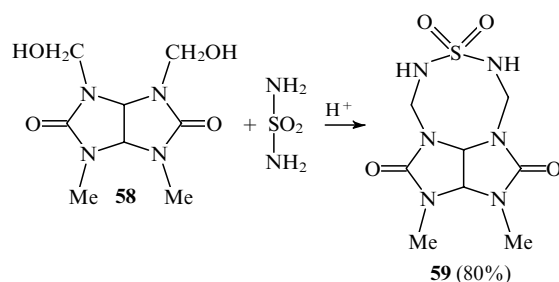
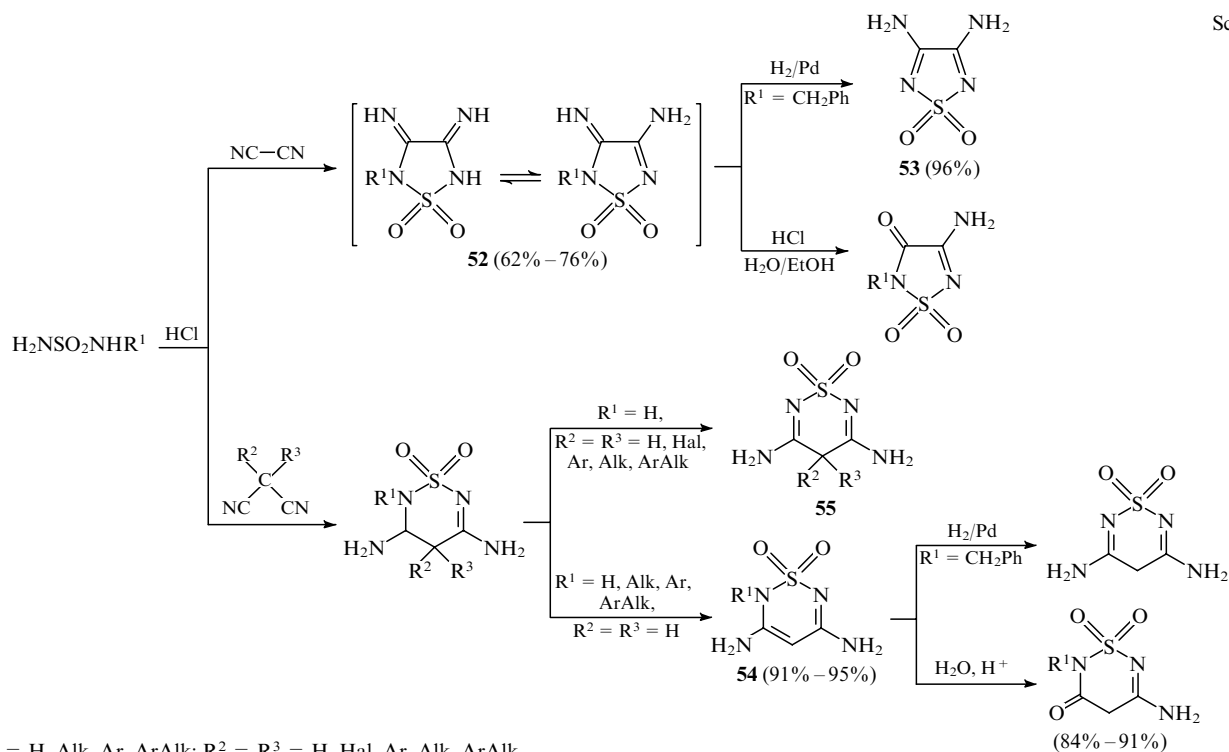
Until recently, condensation of dihydroxy compounds with sulfamides have not found wide use, whereas these reactions with ureas have long been known⁷ and they are successfully used, for example, in the synthesis of bicyclo[3.3.0]octanediones (**16**).

Procedures for the preparation of bi-, tri- and tetracyclic compounds (**57**, **59** and **61**, respectively) containing sulfamide fragments from sulfamides and the corresponding dihydroxy compounds **56**, **58** and **60**, respectively, have been developed in recent years.^{67, 87}

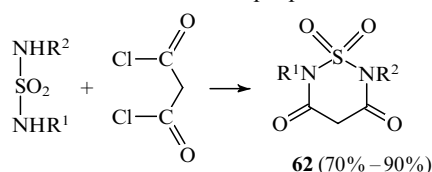


R¹ = Alk; R² = H, Alk.

Scheme 1

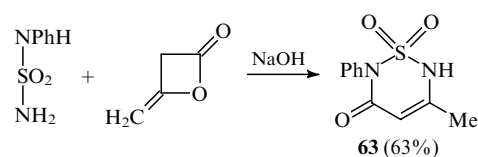


A method for the synthesis of tetrahydro-3,5-dioxo-1,2,6-thiadiazine 1,1-dioxides (**62**) from malonyl chloride and *N*-substituted sulfamides was also proposed.^{35, 88}

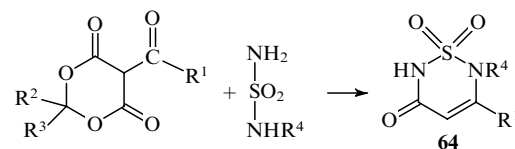


$\text{R}^1 = (\text{CH}_2)_n\text{Ph} (n = 0-2), \text{C}_6\text{H}_{11}; \text{R}^2 = \text{H, CH}_2\text{Ph}$.

An interesting procedure for the preparation of 5-methyl-3-oxo-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxide (**63**) was described.^{89, 90}



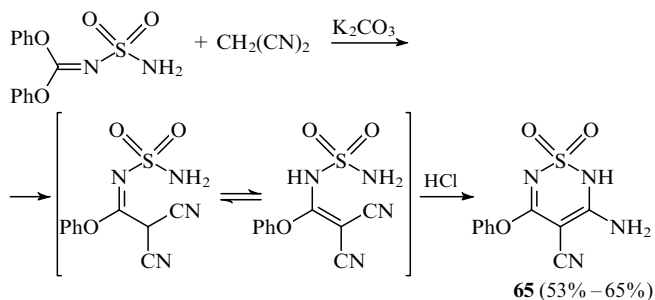
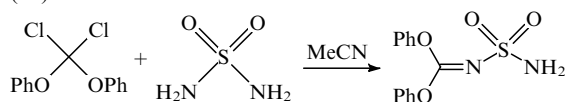
A method for the synthesis of 3-oxo-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxides (**64**) from sulfamides and 5-alkanoyl-1,3-dioxane-4,6-diones was covered by a patent.⁹¹

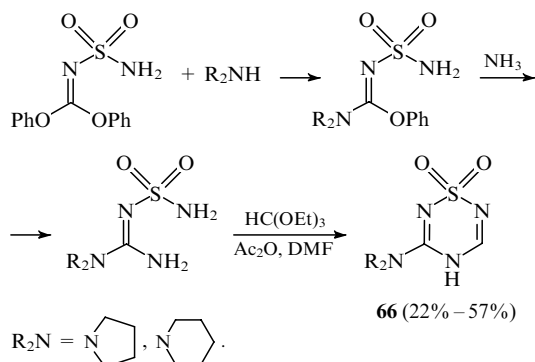


$\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Alk}; \text{R}^4 = \text{H, Alk, Ar}$.

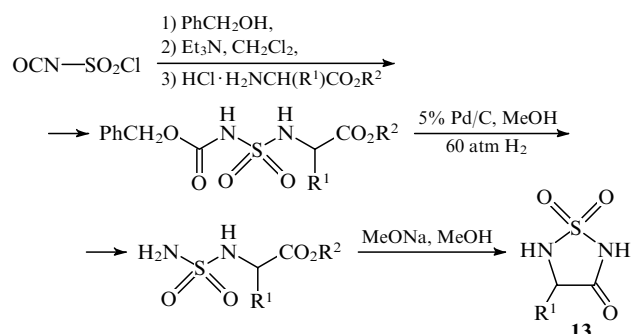
The reactions of derivatives of 1,3-dioxane-4,6-diones with urea and thiourea proceed analogously.⁹²

The use of a new synthon, viz., diphenyl *N*-sulfamoyl-carboimidate, which was prepared from sulfamide and dichlorodiphenoxymethane, opens a new way to the synthesis of 1,2,6-thiadiazine 1,1-dioxide (**65**) and 1,2,4,6-thiadiazine 1,1-dioxide (**66**).⁹³





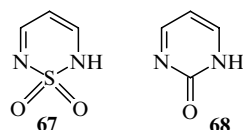
Of the currently available approaches to the construction of cyclic sulfamides, the reactions of sulfonyl halides^{94–98} and chlorosulfonyl isocyanate^{20,99} with amino compounds should also be mentioned. The preparation of 3-oxo-1,2,5-thiadiazolidine 1,1-dioxides (**13**) from chlorosulfonyl isocyanate and amino acids is an example.⁹⁹



The above-considered experimental data demonstrate that sulfamides are rather often similar in their chemical behaviour to ureas. Sulfo-analogues of many urea-containing compounds have been prepared.

IV. Properties of cyclic sulfamides

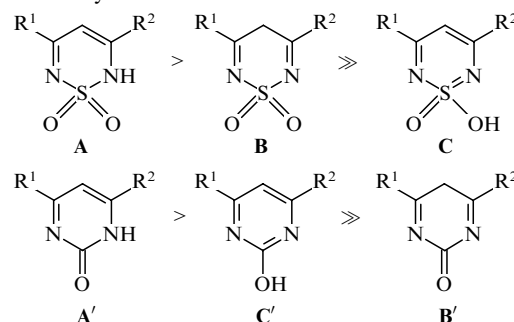
Recently, the aromaticity of heterocyclic compounds has been the subject of many theoretical studies.^{47,49,50} The results of *ab initio* quantum-chemical calculations of the electronic properties and the geometry of these molecules, which were confirmed by X-ray diffraction analysis,^{47,49,50,100,101} demonstrated that the rings in 1,2,5-thiadiazole 1,1-dioxide and 1,2,6-thiadiazine 1,1-dioxide, unlike those in 2-pyrimidinones, are nonaromatic.⁴⁷ The lack of the aromaticity results from the specificity of the structure of the SO₂ group (see Section II). The sulfur atom cannot be involved in π delocalisation because the oxygen and sulfur atoms in thiadiazines (**67**) deviate from the plane passing through the remaining atoms.



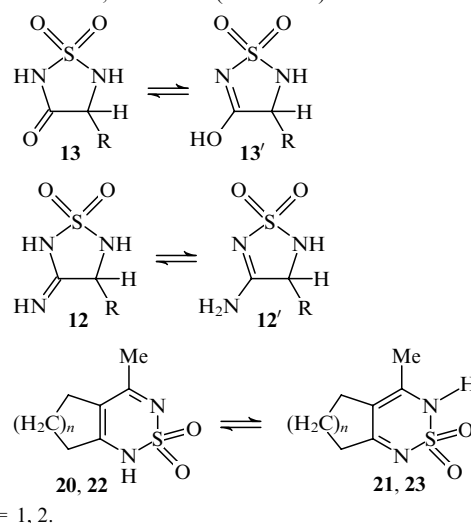
The tautomerism^{39,47,71} and rotational isomerism^{40,102} of cyclic sulfamides attract considerable interest. The difference in the stability of the tautomers of 1,2,6-thiadiazine 1,1-dioxide (**67**) and 2-pyrimidinone (**68**) results from the aromaticity of the compound **68** and nonaromaticity of the compound **67**.⁴⁷

According to the data from X-ray diffraction studies and NMR spectroscopy, 3,5-dialkyl- and 3,5-diaryl-substituted 1,2,6-thiadiazine 1,1-dioxides exist in solutions predominantly as the isomers **A**, whereas the tautomers **B** of 3(5)-hydroxy- and 3(5)-amino-substituted derivatives are more stable.⁴⁷ In no case was

the tautomer **C** experimentally observed. In the case of substituted 2-pyrimidines, the stabilities of tautomers **A'**–**C'** are related in a different way.

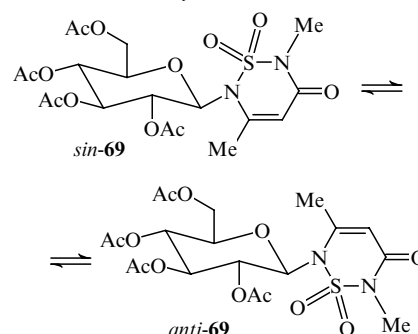


Tautomeric forms of 3-oxo- (**13**) and 3-imino-1,2,5-thiadiazolidine 1,1-dioxides (**12**)³⁹ as well as those of 6,7-dihydro-5*H*-cyclopenta[*c*]- (**20** and **21**) and 5,6,7,8-tetrahydrobenzo[*c*]-2,1,3-thiadiazine 2,2-dioxides (**22** and **23**)⁷¹ were studied.



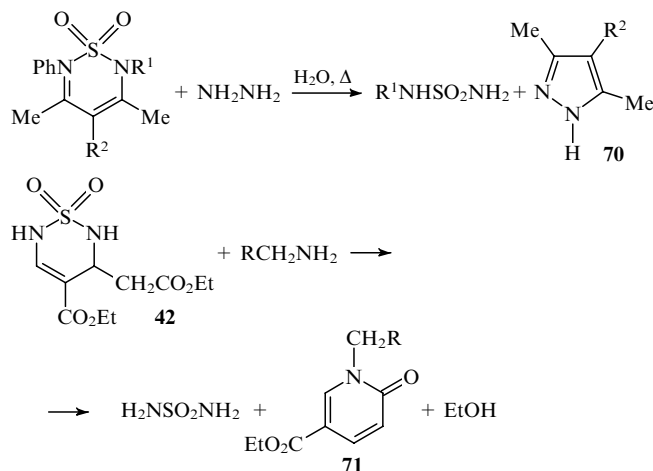
In solution, 3-oxo- and 3-imino-1,2,5-thiadiazoles occur as equilibrium mixtures of the tautomers **12** and **12'** and the tautomers **13** and **13'**, respectively, whereas 6,7-dihydro-5*H*-cyclopenta[*c*]-2,1,3-thiadiazine 2,2-dioxide and 5,6,7,8-tetrahydrobenzo[*c*]-2,1,3-thiadiazine 2,2-dioxide exist predominantly in the forms **21** and **22**, respectively.

The rotational isomerism of glycosylated derivatives of 1,2,6-thiadiazine 1,1-dioxides at the N-glycosidic bond was studied by NMR spectroscopy. Thus 6- β -D-glucopyranosyl-2-methyl-3-oxo-3,6-dihydro-2*H*-1,2,6-thiadiazine 1,1-dioxides (**69**) exist in solutions as mixtures of *syn* and *anti* rotamers.⁴⁰

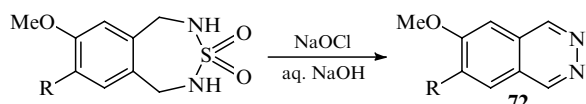


It was found that the energy barriers to rotation about the glycosidic bond for glycosylated thiadiazine derivatives are lower than those for the corresponding uracils and pteridines.^{40,102} This is attributed to the fact that the SO₂ group deviates from the plane of the heterocycle and hinders the rotation about the C–N bond to a lesser extent.

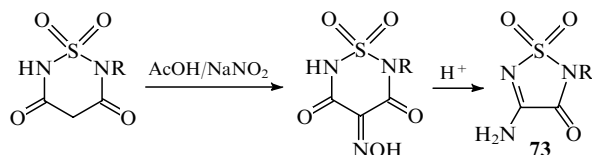
Under the action of various reagents, six- and seven-membered cyclic sulfamides are transformed with elimination of the NSO_2N ,^{103, 104} SO_2 (see Ref. 105) or CO fragments.⁸⁸ Thus derivatives of 1,2,6-thiadiazine 1,1-dioxides were converted under the action of nucleophiles into pyrazoles **70**¹⁰³ and 2-pyridones **71**.¹⁰⁴



Under the action of oxidising agents, seven-membered cyclic sulfamides, which do not contain substituents at the nitrogen atoms were converted into pyridazine derivatives **72** with elimination of the SO_2 fragment.¹⁰⁵



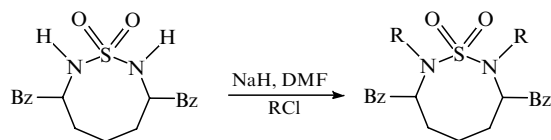
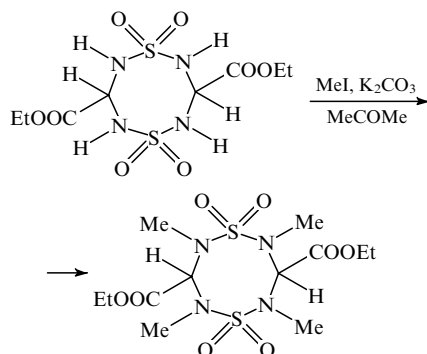
whereas successive nitrosation and acidification of *N*-substituted tetrahydro-3,5-dioxo-1,2,6-thiadiazine 1,1-dioxides afforded 2-substituted 4-amino-2,3-dihydro-3-oxo-1,2,5-thiadiazole 1,1-dioxides (**73**) with elimination of the CO group.⁸⁸



$\text{R} = \text{Ar}, \text{cyclo-C}_6\text{H}_{11}$.

Substitution at the nitrogen atoms is typical of cyclic sulfamides. It was demonstrated that heterocyclic sulfamides undergo alkylation,^{20, 24, 41, 69, 73, 93, 106, 107} acylation,⁶⁹ nitration,⁹⁴ hydroxymethylation,²⁰ silylation^{40, 41, 102} and glycosylation.^{40, 41, 102}

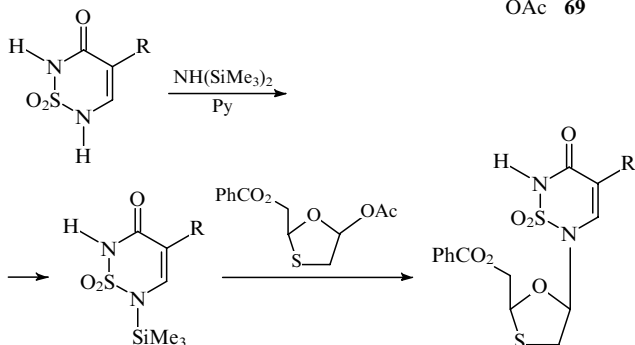
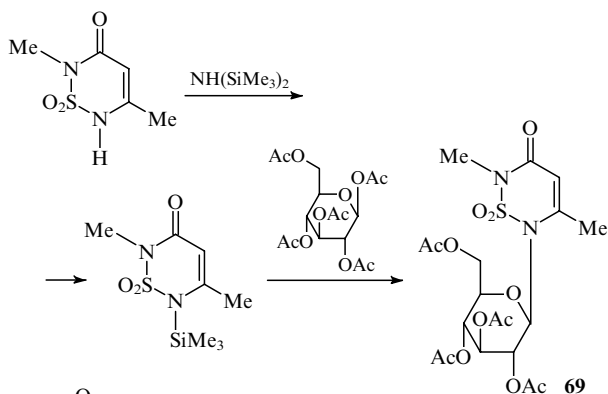
Diazomethane,¹⁰⁶ dimethyl sulfate¹⁰⁷ and alkyl and aryl halides^{20, 24, 41, 69, 73, 93, 107} are used as alkylating agents. Procedures for alkylation with methyl iodide in acetone in the presence of K_2CO_3 or with benzyl chlorides and bromides in the presence of sodium hydride are most generally used.



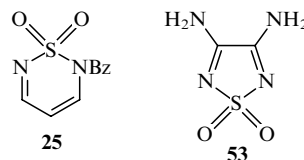
$\text{R} = 4\text{-MeOC}_6\text{H}_4\text{CH}_2$.

1,2,5-Thiadiazolidine 1,1-dioxides were acylated with acyl chloride or dimethylcarbamoyl chloride in an alkaline media,⁶⁹ nitrated with nitric acid⁹⁴ and hydroxymethylated with a methanolic solution of formaldehyde.²⁰

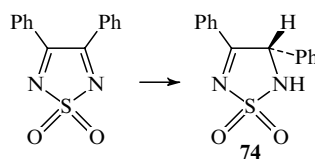
1,2,6-Thiadiazine 1,1-dioxides were silylated with hexamethyldisilazane. Their silyl derivatives underwent glycosylation under the action of penta-*O*-acetyl- β -D-glucopyranose and 1,3-oxathiolane.^{40, 41, 102}



Halogenation and arylation of 1,2,6-thiadiazine 1,1-dioxides **25** ($\text{R}^1 = \text{R}^2 = \text{H}$) at the carbon atom using organometallic reagents have been reported.¹⁰⁸ Amine exchange in 3,4-diamino-1,2,5-thiadiazole 1,1-dioxides **53** has been described.⁸³



The sulfo group is stable to reducing agents.^{5, 43} The SO_2 group also remains intact upon electroreduction. Thus electroreduction of 3,4-diphenyl-1,2,5-thiadiazole 1,1-dioxide in acetonitrile afforded the corresponding dihydrothiadiazole 1,1-dioxide (**74**),¹⁰⁹ i.e., only the $\text{C}=\text{N}$ bond was reduced.



All the above-described reactions are also typical of cyclic ureas. The latter are alkylated with alkyl halides and alkyl sulfates

and undergo acylation, hydroxymethylation, nitration and glycosylation at the nitrogen atoms.^{7, 110–112}

* * *

The examples considered in this review demonstrate that the chemistry of cyclic sulfamides is progressing successfully. Procedures for the preparation of heterocyclic compounds which contain different numbers of carbon atoms in the ring and bear different substituents at the nitrogen and carbon atoms have been developed. One would expect further progress in this field of chemistry. New possibilities of the reactions of sulfamides with carbonyl compounds yielding bi- and polycyclic sulfamides would be expected to be opened. Various useful properties of sulfamides give promise that new approaches to their directed synthesis will be developed.

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Heterophase mechanisms of thermal oxidation of polymers.

New horizons

Yu A Mikheev, G E Zaikov

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Abstract. Based on the results of kinetic analysis of numerous experimental data, advantages of heterogeneous and heterophase mechanisms of autooxidation of non-crystalline polymers over homogeneous liquid-phase mechanisms are demonstrated. The supermolecular organisation of polymer chains according to the pattern of spongy micelles incorporating non-uniform porous areas is chosen as the model structure. It is established that, depending on the physical state of the polymer, the oxidation kinetics correspond either to a mechanism in which reaction chains are distributed over non-uniform nanophases or to a mechanism in which they are mainly located in one nanophase. The kinetic equations obtained for the macroscopic stages of oxidation take into account the dependence of the chemical reactivity of reactants on the thermomechanical mobility of the molecular sponge. It is demonstrated that the fine structure of molecular spongy micelles plays a crucial role in the chemical physics of polymers. The bibliography includes 94 references.

I. Introduction

Oxidation of block polymers is often considered within the framework of homogeneous oxidation schemes designed for liquid hydrocarbons.^{1–13} This is formally based on the view, accepted long ago, that a non-crystalline polymer is an amorphous homogeneous material. The evident physical difference between polymeric and liquid phases is attributed in its simplified form to the functioning of unstable structures continuously formed and degraded and having rather long lifetimes and low rates of the relaxation response to an external action.

Meanwhile, the kinetics of polymer oxidation usually do not fit in the framework of homogeneous reactions. In fact, when analysing the mechanisms of several macroscopic stages (for

example, induction period⁵ and self-accelerated stage^{4–6,8–15}) in terms of homogeneous schemes, researchers were forced either to change the essence of these schemes or to use mathematical simplifications.^{1–17} The results were often at variance with experimental data.

The contradictions caused by the use of the homogeneous reaction model could not fail to cast doubt¹⁶ upon the validity of the mechanisms of inhibited oxidation and ‘critical’ concentrations of antioxidants discussed in the literature.^{4,6–8} Nevertheless, the generally accepted view of the liquid-phase homogeneous structure of a non-crystalline polymeric matrix delayed for a long period the development of an adequate oxidation mechanism, even after the dependence of the reaction rate on the thermomechanical state of the polymeric matrix had been established.^{4–6,18–26} Instead of diverging from the old-fashioned homogeneous model, the researchers spent effort on the improvement of this model. This was done by invoking ideas of polychromatism of kinetic parameters^{5–7} and by assuming the presence of so-called ‘disordered areas’^{4,5} and ‘rigid cages’⁸ in the matrix being oxidised.

The kinetic ‘polychromatism’ assumes that reactions which are elementary in homogeneous media cannot be characterised by a single rate constant when they occur in polymers. It is postulated that the reactivity of particles depends on their closest environment. However, the physical grounds for this dependence usually remain unknown.

The ideas of the molecular-segment ‘disordered areas’ and ‘rigid cages’ make the views on a polymer process somewhat more detailed. It cannot be ruled out that the schemes based on each concept would describe different particular situations. They are unable to serve as the common ground for the simulation of reactions in a non-crystalline polymeric matrix because they assume *a priori* that the ‘areas’ and ‘cages’ arise in an essentially homogeneous medium.

The same is true for the known theoretical approach resorting to the model of propagation of infectious diseases.¹⁴ This approach is based on the statements that oxidation of a partially crystalline polymer develops through multiplication of ‘pest-holes’, which successively involves amorphous regions dispersed inside the crystalline phase, and that the ‘infection’ is transmitted by monomeric oxidation products acting as initiators.

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Since the above approaches are modifications of the same homogeneous reaction model, none of them discloses the physical reasons for, for example, the fact that oxidation of polymer samples in different physical states often follows the same kinetics. Thus the temperature dependence of the rate constant of non-inhibited oxidation of low-density polyethylene (LDPE) in the induction period is described by an Arrhenius equation in the temperature range of 40–200 °C; this implies the absence of changes in the oxidation mechanism on passing from the solid state to the molten state ($T_m \sim 115$ °C).²⁷

The inapplicability of homogeneous schemes (both the classical and modified ones) to the description of the oxidation of polymers is also indicated by the fact that the same polymer often behaves (in the reaction) in different ways depending on the method used to prepare the sample. In addition, the macroscopic stages of polymer oxidation are described by kinetic laws different in kind.

The reasons for these specific kinetic features are hidden in the supermolecular organisation of polymer chains in spongy micelles incorporating non-homogeneous porous areas, *i.e.* in the real heterogeneity of the ‘amorphous’ polymer phase.^{15, 16, 28, 29} The molecular-chain sponge is actually a system of connected pendula (oscillators), the oscillations of which can become cooperated; this makes the units of macromolecules move apart to form nanopores with different widths.

It was emphasised in a series of studies^{15, 16, 18–22} that the initiating activity of admixed initiators and polymeric hydroperoxides and the routes of transformation of free radicals depend on which particular site in the nanoporous structural zone of the molecular spongy matrix contains the reactants. Due to the high degree of heterogeneity and the high elasticity with respect to mechanical treatment, typical of this matrix, stretching of polymer chains and the amplitudes of beating of nanopores of each size can vary over wide limits.

Therefore, the kinetics of oxidation of samples existing in different thermomechanical states, depending on the preparation method, can be different in kind, although the chemical structure of the polymeric molecules remains the same.

II. The influence of the thermomechanical state of a polymer on the oxidation kinetics

1. Characteristic features of the process under structural relaxation conditions

The thermomechanical state of a polymer subjected to oxidation largely depends on the character of thermal and mechanical treatment of the polymer sample prior to the reaction. Oxidation of polymer samples can be described by qualitatively different kinetics depending on the previous history of the samples.

This refers, for example, to samples of isotactic polypropylene (IPP), studied by Pudov *et al.*^{1, 2, 30} and Monakhova *et al.*^{24, 31}

The data on accumulation of polymeric hydroperoxide (POOH) in IPP samples obtained by Pudov *et al.*^{1, 2, 30} (Fig. 1) differ from the results of Monakhova *et al.*^{24, 31} (Fig. 2) by a longer period of accumulation and a lower rate of decomposition of POOH.

The plots for the oxygen absorption rate *vs.* the concentration of accumulated POOH also follow different patterns in these two cases. Pudov *et al.*^{1, 2, 30} attribute this plot to one macroscopic stage and describe it as a sum of two terms close in magnitude

$$v = a [\text{POOH}]^{0.5} + b [\text{POOH}],$$

where a and b are constants. On the contrary, the curves shown in Fig. 2^{24, 31} actually represent three macroscopic stages of oxidation, characterised by different types of variation of v *vs.* $[\text{POOH}]$. In fact, successive transitions from a more or less extensive induction period to a short self-accelerated process and then to a stage with a virtually constant rate of oxygen absorption can be distinguished in curves 3 and 4. At the third stage of oxidation, the concentration of POOH first increases and then starts to decrease.

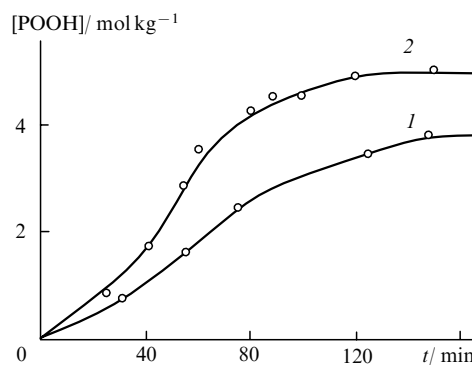


Figure 1. Variation in the concentration of hydroperoxide in films pressed from non-melted IPP powder during oxidation at 130 °C and oxygen pressures of 26.7 (1) and 53.3 kPa (2).^{1, 2, 30}

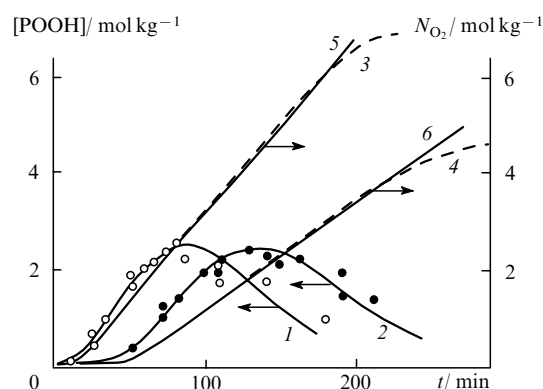


Figure 2. Calculated curves for hydroperoxide accumulation (1, 2) and experimental (3, 4) and calculated (5, 6) curves for the oxygen absorption during oxidation at 130 °C and $P_{O_2} = 40$ kPa of IPP films prepared from the melt and containing small (1, 3, 5) and large (2, 4, 6) spherulites.^{24, 31} The dots correspond to experimental concentrations of POOH.

These kinetic differences are apparently due to nonequivalent methods used to prepare the samples in question. In one study³⁰ films were prepared by short-term (2–3 min) pressing of the IPP powder at 125–130 °C without bringing the crystals to melting, while in the other studies^{24, 31} the initial IPP was first melted at 220 °C and then the melt was cooled to give films with small spherulites. On additional heating, large spherulites were formed but the degree of crystallinity did not change.

It is obvious that pressed films employed by Pudov *et al.*^{1, 2, 30} were characterised by enhanced internal mechanical stress, caused by deformation of the framework of non-melted crystallites and by biaxial orientational stretching of polymer chains which fill the space between the crystallites. Comparison of curves 1, 2 in Fig. 1 with the corresponding curves in Fig. 2 leads to the conclusion that in the concentration range of 0–0.2 mol kg^{−1}, accumulation of POOH in the films prepared by pressing occurs at almost the same rate as in the films with small spherulites. However, the yield of POOH in the subsequent oxidation stages is much higher in the former type of films. This indicates that the reaction rate increases in samples with internal stresses. Apparently, at a certain stage of the process, efficient stress relaxation occurs in ‘stressed’ films, which is accompanied by the appearance of local centres of thixotropic excitation of the matrix.³² In these centres, the frequency and amplitude of beats of macromolecular units increase; this changes the dimensions of nanopores and, consequently, increases the rate of generation of free radicals.^{15–22, 33, 34}

The IPP films prepared by cooling a melt^{24, 31} differed from those made of a pressed conglomerate of non-melted particles by the presence of a much more equilibrated (as regards the thermomechanical state) framework of crystallites. The residual internal

stress in the crystallites is much lower. They are distributed more uniformly in the material and do not bring about any thermomechanical excitation of the matrix or substantial shear deformations during oxidation.

The increase in the induction period associated with enlargement of spherulites due to recrystallisation (see Fig. 2, curve 2) can be explained by assuming that some of the units of macromolecules are incorporated into crystallites and thus induce orientational drawing of the polymer chains in the intercrystallite regions. The stretched polymer chains are fixed rather firmly on the crystallite framework; this accounts for the extension of the induction period.

A similar effect is involved in the oxidation of highly crystalline films of IPP, high-density polyethylene (HDPE) and polymethylpentene subjected to uniaxial orientational drawing. The greater the degree of drawing, the greater the increase in the induction period of oxidation.^{5,35}

The rate of oxidation of LDPE is affected by orientational drawing in a different way. The low degree of crystallinity of this polymer does not ensure sufficient resistance to the internal stress and the fast relaxation increases the oxidation rate from the very beginning of the process.³⁵

Thus, despite the identical treatment of the polyolefin films (orientational drawing), the rates of the initial stage of their oxidation differ depending on the strength of the supermolecular framework.

Yet another specific feature of oxidation of uniaxially stretched IPP films is that the molecular mass of the polymer increases substantially at the initial oxidation stages, whereas in the case of isotropic films, fast destruction of macromolecules is observed.⁵ Calculations have shown³⁵ that the influence of drawing is due to the change in the physical structure of the IPP matrix subjected to oxidation rather than to the change in the solubility and the oxygen diffusion coefficient.

It should be noted that the draw ratio also influences the parameters of the self-accelerated stage of oxidation. This stage becomes longer for high draw ratios;^{5,26,35} in some cases, the rate of oxygen absorption increases according to the law $v \sim \exp(\Phi t)$ rather than in proportion with time.²⁶

The state of the spongy molecular matrix can change due to different types of treatment and thus influence the oxidation kinetics. Thus, it has been reported²⁰ that previous heat treatment of a non-stabilised commercial sample of IPP *in vacuo* decreases the rate of its high-temperature oxidation by increasing the induction period; however, the rate of low-temperature (20 °C) oxidation substantially increases (possibly, due to the structural relaxation under the influence of absorbed moisture²⁹).

Simultaneously, a new specific feature appears which cannot be interpreted within the framework of the homogeneous reaction model, namely, different induction periods are observed for identical contents of POOH in the polymer and, conversely, identical induction periods correspond to hydroperoxide concentrations that differ by an order of magnitude.²⁰

Note that these regularities (observed in the kinetic regime of oxygen absorption) reflect a general feature of heterogeneous micro- and nanoporous materials associated with the lability of their physical structure. In many cases, this lability is undesirable because it accounts for the poor reproducibility of the useful properties of materials.³⁶ The molecular sponge, which is an important structural material of a non-crystalline polymer matrix, exhibits clear-cut susceptibility to thermomechanical treatment and has a fairly labile structure. Owing to these properties of the molecular sponge, non-crystalline polymers differ fundamentally from homogeneous fluids, in which reaction rates do not change upon shear mechanical treatment (stirring). Moreover, parameters of elementary chemical steps proceeding in homogeneous media are usually unambiguous.

2. Specific features of oxidation in the steady state of the polymer matrix

The notion of structural steady state as applied to a polymer being oxidised is somewhat arbitrary. Oxidation is inevitably associated with the formation of oxygen-containing groups in macromolecules and with rupture or cross-linking of polymer chains. These processes change the initial balance of elastic forces in the spongy molecular matrix and cause more or less fast structural evolution. However, if the chemico-mechanical perturbation is relatively slight and the matrix quickly returns to the thermomechanical equilibrium, this process can be regarded as being structurally stationary.

The structurally steady-state oxidation includes several macroscopic stages which obey different kinetic laws. Thus the induction period is characterised by a low rate of oxygen consumption (v_1). This period ends after a small amount of oxygen, usually less than 0.1 mol kg⁻¹, has been absorbed. The v_1 value does not depend on the concentration of hydroperoxide accumulated during the induction period but increases with an increase in the pressure of oxygen without, however, reaching a limiting value²⁰

$$v_1 = \frac{a_1 P_{O_2}}{(b + P_{O_2})^{1/2}},$$

where a_1 and b are constants.

The induction period is followed by a short stage of self-accelerated oxygen absorption. The reaction rate at this stage (v_2) is most often proportional to the oxidation time. In this case, reaction chains are initiated upon dissociation of POOH and are terminated upon recombination of macropoxylys.

As oxidation develops, the increase in the rate of oxygen absorption becomes less pronounced. After some period, the rate reaches a maximum and no longer depends on the POOH concentration. Whereas in the first stage (v_1), the rate of oxygen absorption does not reach any limiting value upon an increase in the pressure of oxygen, in the third stage (v_3) this rate does have a limit. It is significant that the third stage of oxidation is established earlier than the maximum hydroperoxide concentration has been attained and continues even after the POOH concentration has considerably diminished. This pattern (which can be seen, for example, in Fig. 2) is typical of reactions having the zero order with respect to hydroperoxide.^{20–22} This distinguishes high-molecular-mass block polymers from their solutions.

The difference between the kinetics of oxidation of block and dissolved LDPE is demonstrated in Fig. 3 (data of Ref. 37). Although curves 1'–3' are qualitatively similar, the kinetics of accumulation of POOH in the two systems are substantially different. It can be seen that the variation of the hydroperoxide concentration in the melt is described by a curve with a sharp maximum (curve 1'), while that in solution is described by monotonic curves with relatively low limiting values (curves 2', 3').

According to a study by Iring *et al.*,³⁷ oxidation of LDPE in solutions can be described by a kinetic equation for liquid-phase oxidation

$$\frac{d[\text{POOH}]}{dt} = \alpha v - k[\text{POOH}], \quad (1)$$

where α is the yield of POOH, v is the rate of oxygen absorption and k is the rate constant for the decomposition of POOH. The reaction reaches a steady-state regime at those degrees of conversion at which the consumption of the CH groups is still insignificant and the following conditions hold:

$$\left(\frac{d[\text{POOH}]}{dt} \right)_{\text{lim}} = 0, \quad \alpha v_{\text{lim}} = k[\text{POOH}]_{\text{lim}} \rightarrow \text{const.}$$

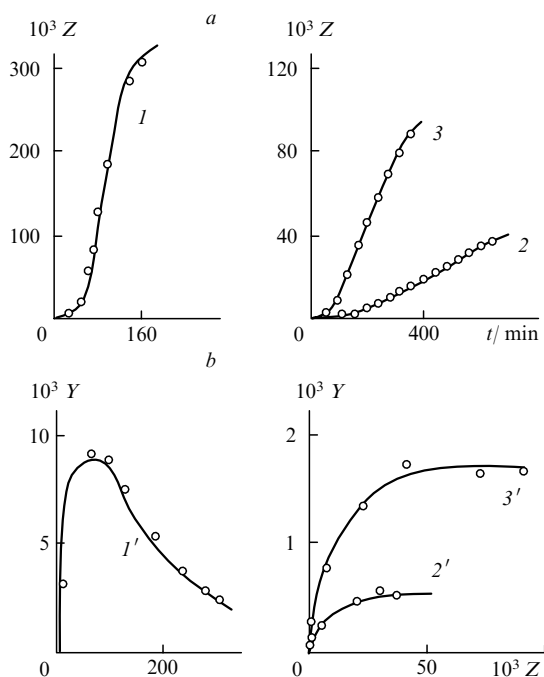


Figure 3. Amount of absorbed oxygen (Z , moles of O_2 per mole of molecular units) vs. oxidation time (a) and amount of accumulated hydroperoxide (Y , moles of POOH per mole of molecular units) vs. amount of absorbed oxygen (b) during the oxidation of a melt ($1, 1'$) and a solution of LDPE (the LDPE concentration is $0.56 \text{ mol litre}^{-1}$) in trichlorobenzene ($2, 2', 3, 3'$).³⁷ Temperature/ $^{\circ}\text{C}$: $1, 1', 2, 2'—160, 3, 3'—170$. Pressure of O_2 /kPa: $1, 1'—100; 2, 2', 3, 3'—75$.

Oxidation in the melt also reaches a steady-state regime at a relatively low consumption of CH groups (Fig. 3, curve 1); however, the pattern of variation of the POOH concentration (Fig. 3, curve $1'$) differs from that for the liquid-phase reaction.

Oxidation of high-molecular-mass block polyolefins in the steady-state regime is characterised by the following features.^{15, 20–22}

- (1) hydroperoxide is not the only molecular product of the reaction (other oxygen-containing compounds are also formed);
- (2) decomposition of POOH is due to its reaction with an oxidation product and is not accompanied by the formation of free radicals;
- (3) oxidation has the zero order with respect to hydroperoxide.

It should be emphasised that the zero order with respect to hydroperoxide in the steady state has been repeatedly found by numerous researchers; however, this fact has not received adequate attention (apparently, in the heyday of the theory of liquid-phase oxidation of hydrocarbons, researchers have not yet faced the problem of structure-kinetic modelling). Since this finding was undoubtedly significant, it was specially verified in relation to the oxidation of molten polyethylene oxide (PEO),^{15, 18, 19} a high-elasticity copolymer of ethylene with propylene and solid-like IPP.²¹ These experiments confirmed simultaneously yet another fact which had been repeatedly described previously — admixed initiators present in polymers accelerate the attainment of the highest reaction rate but do not influence the rate itself over a broad range of concentrations.

Figure 4 presents experimental results on the oxidation of a PEO melt in air.¹⁵ It can be seen that the constant rate v_3 is established earlier (curve 1) than the maximum POOH concentration is attained (curve 2). The curves for the consumption of the polymer CH groups (curve $1'$) and for the accumulation of aldehyde reaction products (curve $2'$) also indicate that constant

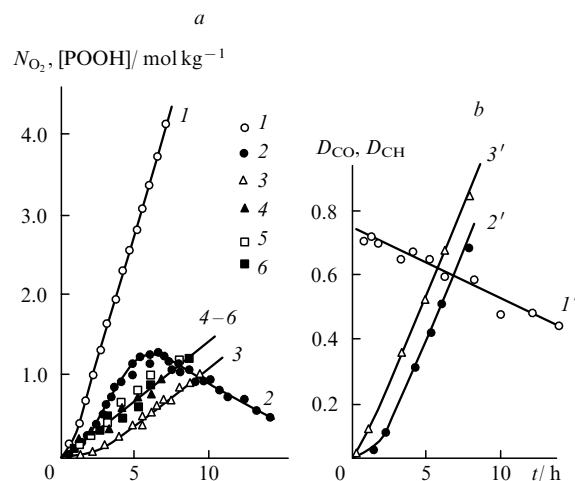


Figure 4. Curves for oxidation of molten poly(ethylene oxide) at 90 ($1, 2, 1'–3'$) and 80 $^{\circ}\text{C}$ ($3–6$); (a) oxygen absorption (1) and hydroperoxide accumulation ($2–6$); (b) variation of the optical density of the CH ($1'$) and CO ($2', 3'$) absorption bands in the IR spectra. Concentration of dibenzoyl peroxide/ mol kg^{-1} : 0 ($1–3, 1', 2'$), 0.06 ($3'$), 0.0165 (4), 0.039 (5) and 0.12 (6). The IR spectra were recorded using chloroform solutions of the polymer (10 mg ml^{-1}) (data from Refs 15, 18).

oxidation rates are rapidly attained and that they do not depend on the content of POOH in the melt.

The introduction of a foreign initiator, dibenzoyl peroxide (BP) in concentrations of up to 0.12 mol kg^{-1} , into the PEO melt eliminates the self-accelerated stage but does not influence the steady-state rates of accumulation of aldehyde (curve $3'$ in Fig. 4 is parallel to the straight section in curve $2'$) and hydroperoxide (curves $4–6$ are parallel to the straight section in curve 3).

The fact that the steady-state rate of oxidation does not depend on the content of a foreign initiator indicates that the polymeric matrix has some structural filter ('bottle-neck'), which restricts the transfer of free radicals from areas in which the initiator dissociates to other areas in which chain oxidation occurs.

It is noteworthy that dibenzoyl peroxide present in a relatively high amount in a PEO melt depresses the reaction; as its concentration increases from 0.12 to 0.38 mol kg^{-1} , the rate v_3 diminishes 1.4 fold at 90 $^{\circ}\text{C}$,¹⁹ which is inconsistent with the homogeneous model.

The 'bottle-neck' effect is clearly manifested in the experiments on oxidation of solid-like IPP in the presence of dibenzoyl peroxide.²¹ Figure 5 shows how the total concentrations of BP being consumed and POOH being accumulated vary during the

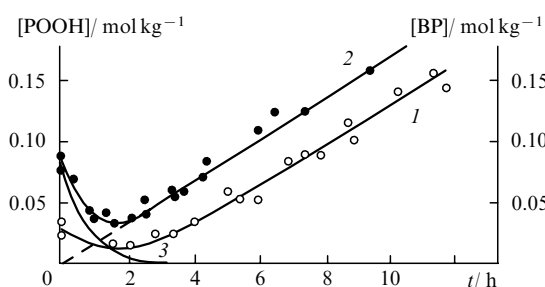


Figure 5. Variation of the total concentration of hydroperoxide and dibenzoyl peroxide ($1, 2$) and the concentration of only dibenzoyl peroxide (3) during oxidation of IPP films in air at 100 $^{\circ}\text{C}$.²¹ $[\text{BP}]_0/\text{mol litre}^{-1}$: (1) 0.025 , ($2, 3$) ~ 0.8 .

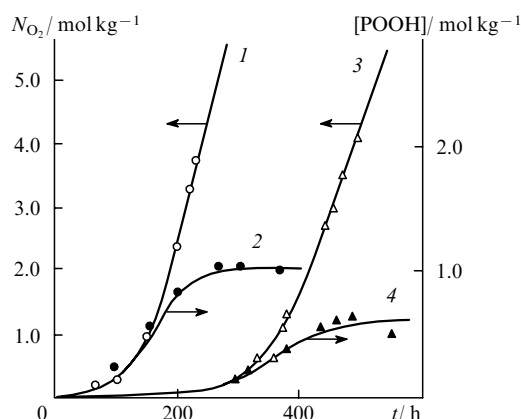


Figure 6. Amount of the absorbed oxygen (1, 3) and accumulated hydroperoxide (2, 4) vs. time of oxidation of low-molecular-mass APP with $M_n = 4500$ (1, 2) and 5-fold orientationally drawn IPP films (3, 4) at $T = 120^\circ\text{C}$ and $P_{\text{O}_2} = 10^3\text{ kPa}$.²⁶

oxidation of IPP films in air at 100°C . In this particular case, the presence of a structural filter for the radicals arising is quite obvious: the higher the content of BP in the polymer, the greater fraction of BP decomposes unproductively with respect to the accumulation of POOH. In addition, the steady-state rate of the process does not depend on the initial concentration of BP or on the current concentration of POOH.

Yet another result obtained in a study of oxidation of a low-viscosity melt of atactic polypropylene (APP) with the molecular mass $M_n = 4500$ and orientationally drawn IPP films (Fig. 6) is worth noting.²⁶ The rate of oxidation at 120°C increases for a long period in direct proportion to the concentration of the accumulating POOH; simultaneously, the amount of absorbed oxygen increases with time according to an exponential law and $v \sim \exp(\Phi t)$. The same pattern is followed at 110 and 130°C . Meanwhile, oxidation of solutions of these polymers in inert trichlorobenzene (concentration 0.56 mol kg^{-1} per monomer unit) obeys kinetic laws of homogeneous reactions, *i.e.* the dependences $v \sim t$ and $v \sim [\text{POOH}]^{0.5}$ hold. Thus, the kinetics of oxidation of polymer samples in which the molecular sponge exists in the state of enhanced thermal fluctuation mobility differ from the kinetics of oxidation of liquid hydrocarbons or high-molecular-mass polyolefins in the structural steady state.

To summarise, it can be noted that oxidation of the same (from the chemical viewpoint) polymer is described, depending on its thermomechanical state, by a whole range of kinetic laws different in kind, which is inconsistent with the model of homogeneous reactions. Thus a new model taking into account the nanosize heterogeneity of the non-crystalline polymeric phase needs to be developed.

III. The microreactor model and kinetic regimes of oxidation

In several studies,^{15, 16, 18–22, 28, 29, 33, 34, 38, 39} non-crystalline polymers are considered as systems of molecular-chain spongy micelles which fill the cells of an infinite three-dimensional framework (Fig. 7a). This framework is an open-work lattice of paracrystalline domains, each of them containing up to a dozen parallel segments. The size of spongy micelles is of the order of tens of nanometers. The three-dimensional framework in the matrix of partially crystalline polymers incorporates a more or less shaped carcass of lamellar crystallites (Fig. 7b).

The molecular spongy micelle, which acts as a chemical microreactor, is a heterophase aggregate, the chains of which enter the paracrystalline domains at one end and enter the spongy grains at the other end. The chains within the grain are tightened by cohesion forces but are not completely collapsed, being

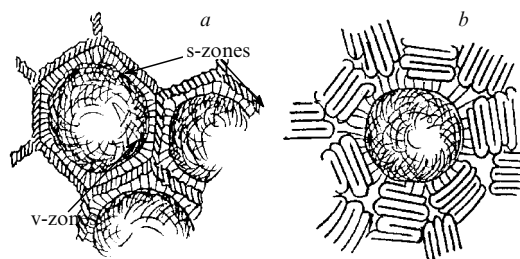


Figure 7. Scheme of the molecular spongy-micellar nanosized reactor for non-crystalline (a) and partially crystalline (b) polymers.

stabilised as a sponge filled with fairly narrow micropores (more precisely, nanopores). The sizes of the micropores range from a chemical bond length to a polymer chain thickness ($0.1–0.5\text{ nm}$).

Under conditions of balanced elastic forces between the spongy grain and the domains of the continuous framework, a layer is formed consisting of radially arranged chain segments, which constitute the walls of relatively wide nanopores (supernanopores). As a consequence, two types of nanosized zones arise in the micelle, namely, s-zones consisting of radial chain segments (the size of a thermodynamic segment is $2–3\text{ nm}$), which form supernanopores, and v-zones consisting of grains with narrow nanopores.

The chain segments of these two zones are characterised by different motion dynamics. The segments in the s-zones play a role of mechanical strings fixing the micellar grain; the s-zones themselves can be compared to a porous adsorbent with a rigid framework. A v-grain is close in thermomechanical properties to a mobile drop of a liquid. Such a drop hanging from a domain of the continuous three-dimensional framework can execute, to a certain extent, its own vibrational or rotational motions and volume beats, thus transferring the kinetic momentum to more or less flexible polymer chains composing the drop.

Due to their spongy structure, the micelles can rapidly rearrange and capture even those admixtures where the molecules are larger than the diameter of empty nanopores. In addition, since the molecular sponge is, in essence, a set of coupled pendula, it is subject to interference, *i.e.*, damping or synchronisation of oscillations; this creates conditions for a fluctuation increase in the size of v-nanopores or, correspondingly, for more or less fast migration of admixtures over the sponge bulk.

The nanosized heterogeneity of the molecular spongy micelles influences the chemistry of chain reactions. Firstly, foreign compounds (oxygen, initiators, inhibitors) are distributed non-uniformly between the zones, being mainly accumulated in the v-grains. Secondly, due to different sizes of the s- and v-nanopores, the reactivities of macromolecules and admixtures absorbed in them are appreciably dissimilar. Indeed, a reacting species in a narrow v-micropore resides most of the time under constrained conditions — either on a nanopore wall (if it belongs to the macromolecule) or in the pore bulk (if it is a foreign species). A foreign molecule is expelled to the pore bulk under the influence of dispersion electromagnetic forces.^{28, 29} The situation in an s-nanopore is different: most of the time, a foreign molecule is adsorbed on the walls of a pore.

The difference between the chemical reactivities of a species caused by the steric and energetic nonequivalence of s- and v-nanopores affects all the intermediates of a chain reaction. The quantitative changes in the reactivity of the same reactant can be very pronounced; the pathways of transformations in the two zones can differ even qualitatively.

Chain reactions in spongy micelles can proceed in different modes; kinetic modelling can be performed most easily for the steady-state heterophase and homophase modes, which are realised in the pure form when the rate of structural evolution is negligibly low, *i.e.* when the volumes and the properties of the zones are virtually invariant.

By definition, the scheme of a heterophase process should include separate charts for the reactions in each zone and the chart for the transfer of the reacting species from one zone to another. The primary reactions occur usually in s-zones because these zones provide more favourable conditions for the dissociative generation of free radicals, which subsequently migrate to v-zones.

If a chemical reaction is localised in one zone, it can formally be referred to as a homophase reaction. This situation is observed, for example, when free radicals are generated in v-zones when v-nanopores undergo high-frequency fluctuations and thus reach the size of s-nanopores. In this case, the initiating activity of the POOH groups captured by v-nanopores increases and the fluctuation initiation of a chain reaction starts to prevail.

The heterophase mode, involving coupling of non-uniform reaction chains, is more frequently encountered in the absence of clear-cut structural evolution of high-molecular-mass polyolefins. Oxidation of a polymer without an admixed initiator starts upon direct reaction of oxygen adsorbed on s-nanopore walls with the CH groups of the polymer s-segments. The greater part of the generated free radicals enter into subsequent reactions and decay without leaving the s-nanopore. When a small portion of radicals has passed from s-zones to the bulk of v-grains and has induced there reaction v-chains, the process acquires a heterophase character.

The sequence of s,v-transitions (s,v-translations) of free radicals described by the corresponding chart means physically the passage of free valences through the structural 'bottle-neck'. The 'bottle-neck' capacity depends on the thermomechanical state of the polymer sample and on the presence of impurities able to promote or, conversely, suppress the s,v-translation of free valences.

The secondary reaction chains induced by this transfer (in v-zones) differ fundamentally from the primary chains (in s-zones) in the character of transformations. In particular, oxygen is mainly accumulated in v-zones. In addition, the rate of rupture of polymer chains with participation of alkyl macroradicals and the rate of termination of oxidation chains in v-zones are lower than those in s-zones. Consequently, the reaction v-chains are longer. Thus, the amount and composition of the oxidation products are mainly determined by the transformations of polymer units of v-zones, which constitute the main bulk of the molecular spongy micelles.

The steady-state oxidation mode includes the steps of transfer of hydroperoxide groups from v-zones to s-zones. The hydroperoxide formed in narrow v-nanopores dissociates into radicals very slowly due to unfavourable steric and energetic conditions. However, as hydroperoxide is accumulated, it starts to occupy the stationary s-zones, which have supernanopores favourable for dissociation. Thus the process passes from the induction period to the self-accelerated stage.

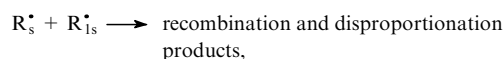
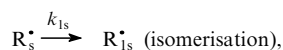
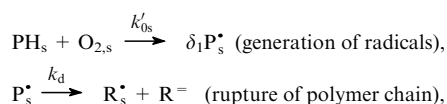
IV. Kinetic model of oxidation of polyolefins

1. Induction period

In accordance with the foregoing, the overall scheme of an initial period of autooxidation of polyolefins includes two charts for reactions in s- and v-zones and a chart for the inter-zone chemical induction, responsible for coupling of inhomogeneous reaction chains.

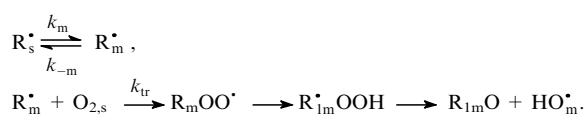
In the absence of a foreign initiator, free radicals are generated in s-nanopores upon the reaction of oxygen with the CH groups of the polymer.

The scheme of the primary reaction chain (in the s-zone) can be written in the following general form:



where PH_s is a polymer unit in zone s, which includes reactive hydrogen atoms, $\text{P}_s^\bullet$ is the macroradical with a free valence on an internal unit of the macromolecule [for polyethylene (PE), this is $\sim\text{CH}_2\dot{\text{C}}\text{H}\sim$ and for polypropylene (PP), these are $\sim\text{CH}_2\dot{\text{C}}(\text{CH}_3)\sim$ and $\sim\dot{\text{C}}\text{HCH}(\text{CH}_3)\sim$], δ_1 is a factor characterising the yield of free radicals, $\text{R}_s^\bullet$ and $\text{R}^\bullet$ are a terminal radical and a terminal unsaturated group, respectively, and $\text{R}_{1s}^\bullet$ is the product of isomerisation of the terminal radical $\text{R}_s^\bullet$ (the structures of $\text{R}_s^\bullet$ and $\text{R}_{1s}^\bullet$ for PP have been considered previously²¹).

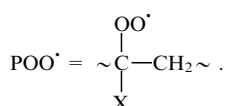
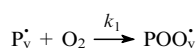
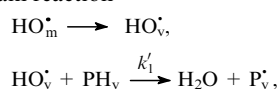
The pattern of the inter-zone transfer of free valence includes migration of the radical $\text{R}_s^\bullet$ from the supermolecular framework structure to the s-nanopore bulk (with transition to the $\text{R}_m^\bullet$ state) and subsequent oxidation of $\text{R}_m^\bullet$:



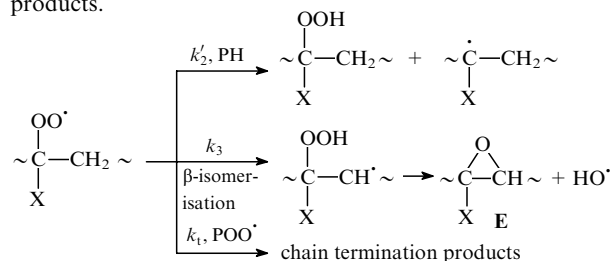
The subscript 'm' implies belonging to the nanopore bulk and 'tr' stands for belonging to the inter-zone chain transfer process.

As noted above, the rate of the s,v-transfer is negligibly low compared to the rate of radical transformations in the s-zone. It is determined by the thermomechanical ability of the radicals $\text{R}_s^\bullet$ to oscillate with some frequency between the rigid framework of s-segments and the s-nanopore bulk and to pass to the state $\text{R}_m^\bullet$, more convenient for the reaction with oxygen. The terminal radical $\text{R}_m\text{OO}^\bullet$ thus formed undergoes α -isomerisation⁴⁰ to a hydroperoxyalkyl radical, which decomposes with elimination of free hydroxyl $\text{HO}_m^\bullet$.

The free hydroxyl migrates to the v-zone and induces there a chain reaction

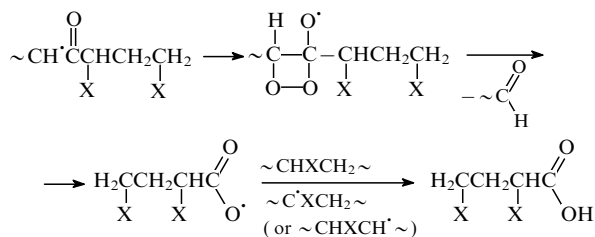


The $\text{POO}_v^\bullet$ radical thus formed can be converted according to three pathways to give hydroperoxides, epoxides, or chain termination products.



Epoxides **E**, which are highly reactive towards free radicals, undergo subsequent transformations giving rise to carbonyl compounds (the corresponding reactions are considered below).

When calculating the s-scheme, we employed the condition of steady-state concentration of free radicals and did not take into account the loss of s-radicals by the inter-zone transfer; however, this transfer needs to be taken into account (as an initiation step) in the calculation of the v-scheme. The concentration of macroradicals responsible for the inter-zone chemical induction can be described by the expression



The presence of some compounds such as methyl ethyl ketone, methyl propyl ketone, butyraldehyde, pentanone, hexanone, *etc.* among the products of oxidation of polyolefins proves the occurrence of the above reactions.^{41–43}

The transformations of the terminal radical **B**[•] are shown in Scheme 2.

This set of reactions, which is far from being complete, is still sufficient to demonstrate the pathways to the final products of polyolefin oxidation and to state the fact that transformations of radicals **A**[•] and **B**[•] and carbonyl compounds have no influence on the steady-state concentration of peroxy radicals [Eqn (2)]. The concentration of carbonyl compounds, which are oxidised and formed again in the chain process, continuously increases.

In view of the foregoing, one can write the following condition for the steady-state concentration of epoxide

$$\frac{d[\text{E}]}{dt} = k_3[\text{POO}^{\cdot}]_1 - k_4[\text{E}][\text{POO}^{\cdot}]_1 = 0, \quad (4)$$

where $k_4 = (k'_4 + k''_4)$. It follows from Eqn (4) that $[\text{E}] = k_3/k_4 = \text{const}$. The total rate of accumulation of carbonyl compounds (CO) in the epoxide branch of the reaction is equal to

$$v_{\text{CO},1} = \left(\frac{d[\text{CO}]}{dt}\right)_1 = (\alpha_1 + \alpha_2)k_4[\text{E}][\text{POO}^{\cdot}]_1 = \alpha k_3[\text{POO}^{\cdot}]_1,$$

where α_1 and α_2 are the yields of polymeric and volatile compounds, respectively, and α is their sum. Thus, after condition (4) has been reached, the rate $v_{\text{CO},1}$ depends on the pressure of oxygen in the same way as the rates v_1 and $v_{[\text{POOH}]_1}$ and the content of CO groups increases with time in accordance with the equation

$$[\text{CO}]_1 = v_{\text{CO},1} t. \quad (5)$$

The same is true for the growth of the concentration of broken polymer chains (n) in the v-zones of spongy micelles detected by viscometry. The total rate of chain rupture is composed of two fractions proportional to the constants k'_4 and k''_4 :

$$v_{n,1} = \left(\frac{dn}{dt}\right)_1 = (v_1 k'_4 + v_2 k''_4)[\text{E}][\text{POO}^{\cdot}]_1 = \text{const}[\text{POO}^{\cdot}]_1, \quad (6)$$

where v_1 and v_2 are coefficients.

The direct proportionality between the amount of oxidation products and the amount of oxygen absorbed in the induction

period, which follows from the scheme in question, is also retained for some time after the induction period has been completed, this time being much longer for the processes of accumulation of carbonyl compounds and destruction of macromolecules than for accumulation of POOH.^{41–43}

It should be emphasised that Eqn (5) refers to the overall process of formation of carbonyl compounds accompanied by abstraction of monomeric fragments. These destruction steps change the viscosity of the polymer solution only slightly compared to the primary scission steps in the epoxide branches, the rates of which are described by Eqn (6).

2. Hydroperoxide-initiated process

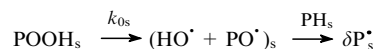
The induction period in the autooxidation of polyolefins usually ends when 10^{-2} mol kg⁻¹ of oxygen has been absorbed due to the occupation of the s-zones of the spongy matrix by the hydroperoxide from v-zones. This occupation is provided by the transfer of free valence and migration of OOH groups along the polymer chain and by the fluctuation steps of rearrangement of the molecular sponge units.^{15, 20, 21, 33}

By expressing the total frequency of the v,s-transfer of the OOH groups in terms of the effective constant k_{vs} , taking into account the fact that activation of these processes requires a fluctuation of the sponge with opening of narrow v-micropores, we can express the scheme of the hydroperoxide v,s-transfer as

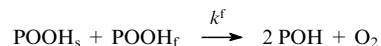


where the subscript 'f' refers to a fluctuationally excited v-nanopore with a trapped OOH group.

Having got into the s-nanopores, the OOH groups become able to dissociate to give free radicals



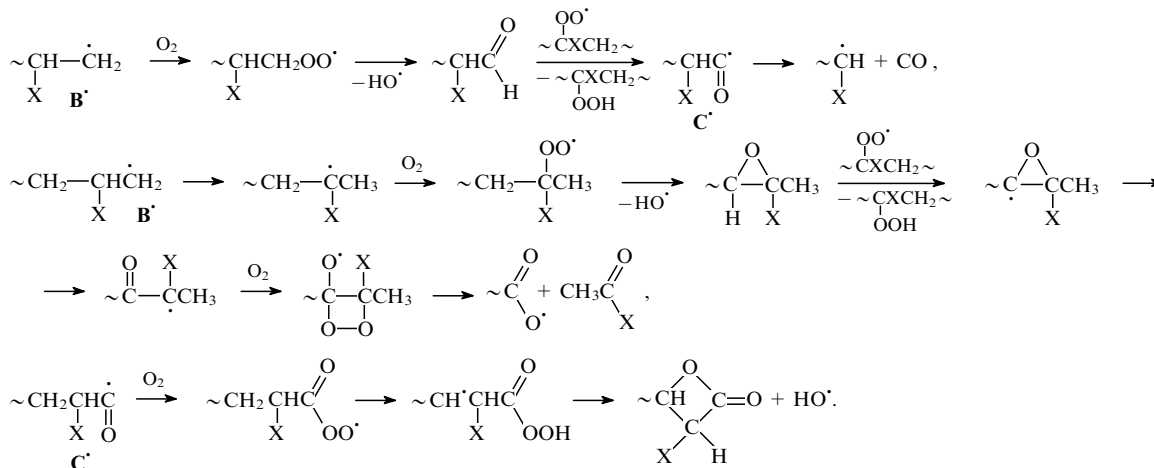
and, as their concentration increases, to enter into the bimolecular reaction



giving no free radicals. This scheme of the chemical inter-zone feedback permits us to express the steady-state concentrations of the OOH groups in the fluctuationally active and s-states by the equation

$$\begin{aligned}
 \frac{d[\text{POOH}]_f}{dt} &= k_f[\text{POOH}]_v - k_{-f}[\text{POOH}]_f - \\
 &- k_{vs}[\text{POOH}]_f - k^f[\text{POOH}]_s[\text{POOH}]_f = 0.
 \end{aligned}$$

Scheme 2



In view of the high rate of deactivation of fluctuations, the last two terms can be neglected and the resulting expression

$$[\text{POOH}]_f = \frac{k_f[\text{POOH}]_v}{k_{-f}}$$

can be used in the equation for the rate of the reaction involving s-hydroperoxide

$$\frac{d[\text{POOH}]_s}{dt} = k_{vs}[\text{POOH}]_f - k_f[\text{POOH}]_s[\text{POOH}]_f - k_{os}[\text{POOH}]_s = 0.$$

The concentration $[\text{POOH}]_s$ found in this way,

$$[\text{POOH}]_s = \frac{k_{vs}k_f[\text{POOH}]_v}{k_{-f}k_{os} + k_fk_f[\text{POOH}]_v}, \quad (7)$$

can be used to express the overall rate of radical generation in s-zones by the equation

$$v_{is} = k_0''[\text{O}_{2,s}] + \delta k_{os}[\text{POOH}]_s \approx \delta k_{os}[\text{POOH}]_s.$$

The contribution of the direct reaction between CH bonds and oxygen soon becomes negligibly small and the expression for $v_{tr,1}$ derived previously is replaced by the equation

$$v_{tr,2} = \frac{k_{tr}k_m\delta k_{os}[\text{POOH}]_s[\text{O}_{2,s}]}{2k_{1s}(k_{-m} + k_{tr}[\text{O}_{2,s}])}$$

(the subscript 2 denotes the second stage of the oxidation process).

The equation describing the concentration of peroxy radicals also changes

$$[\text{POO}^*]_2 = \frac{(k_{tr}k_m\delta k_{os}[\text{POOH}]_s[\text{O}_{2,s}])^{0.5}}{[4k_1k_{1s}(k_{-m} + k_{tr}[\text{O}_{2,s}])^{0.5}]}. \quad (8)$$

During an initial period of the accelerated stage of autooxidation, the final reaction products are accumulated synchronously with the hydroperoxide. Being unable to dissociate in the v-zones of the spongy matrix, hydroperoxide is accumulated for some period almost without reacting with other oxidation products because their concentrations are too low. The rate of hydroperoxide accumulation during this period is described by the equation

$$v_{[\text{POOH}]_2} = k_2[\text{POO}^*] = A(\delta k_{os}[\text{POOH}]_s)^{0.5},$$

where

$$A = k_2 \left\{ \frac{k_{tr}k_m[\text{O}_{2,s}]}{4k_1k_{1s}(k_{-m} + k_{tr}[\text{O}_{2,s}])} \right\}^{0.5},$$

or, with allowance for Eqn (7) and the relation $[\text{POOH}]_v \approx [\text{POOH}]$, which means that the major portion of OOH groups of the non-crystalline polymer phase is concentrated in the v-zones, by the equation

$$v_{[\text{POOH}]_2} = A \left\{ \frac{\delta k_{os}k_{vs}}{k_f[1 + k_{os}k_{-f}/(k_fk_f[\text{POOH}]_v)]} \right\}^{0.5} = \frac{v_{[\text{POOH}]_3}}{(1 + C/[\text{POOH}])^{0.5}}, \quad (9)$$

where $v_{[\text{POOH}]_3} = A(\delta k_{os}k_{vs}/k_f)^{0.5}$, $C = k_{os}k_{-f}/(k_fk_f)$.

The expressions for the rates of the other macroscopic processes have the following form:

$$\begin{aligned} v_{CO} &= \alpha k_4[E][\text{POO}^*] = \frac{v_{CO,3}}{(1 + C/[\text{POOH}])^{0.5}} = \\ &= \frac{\gamma v_{[\text{POOH}]_3}}{(1 + C/[\text{POOH}])^{0.5}}, \\ v_{aq} &= k'_1[\text{HO}^*][\text{PH}] = \beta k_3[\text{POO}^*] = \frac{v_{aq,3}}{(1 + C/[\text{POOH}])^{0.5}}, \end{aligned} \quad (10)$$

$$\begin{aligned} v &= v_{CO} + v_{[\text{POOH}]_2} = \frac{v_3}{(1 + C/[\text{POOH}])^{0.5}} = \\ &= \frac{v_{[\text{POOH}]_3}}{\varphi(1 + C/[\text{POOH}])^{0.5}}, \end{aligned} \quad (11)$$

$$v_n = (v_1k'_4 + v_2k''_4)[E][\text{POO}^*] = \frac{v_{n,3}}{(1 + C/[\text{POOH}])^{0.5}}, \quad (12)$$

where $\gamma = \alpha k_3 k_2^{-1}$, β is the yield of water, φ is the yield of the hydroperoxide, $v_{[\text{POOH}]_3}$, $v_{CO,3}$, $v_{aq,3}$, v_3 and $v_{n,3}$ are the maximum rates at the third macroscopic stage of autooxidation, attained when $C/[\text{POOH}] < 1$. This inequality transforms Eqn (7) to the form

$$[\text{POOH}]_s = \frac{k_{vs}}{k_f} = \text{const}. \quad (13)$$

It follows from Eqn (13) that the self-accelerated stage of oxidation should sooner or later come to an end because the s-zone is the structural boundary of the micellar reactor, which terminates the chemical relay of the OOH groups and thus favours the bimolecular reaction giving no free radicals.

Since a hydroperoxide-involving reaction takes place in the s-zone, oxidation takes place again in a regime which obeys a zero order with respect to hydroperoxide. In this case, hydroperoxide still acts as an initiator and simultaneously plays the role of a specific buffer because it maintains a constant rate of initiation of the reaction v-chains and a certain time-independent concentration of free peroxy radicals [Eqn (8)].

Equations (9)–(11) and (13) derived theoretically have been confirmed experimentally in a number of studies^{15, 18, 20–22} in which the third macrokinetic stage of autooxidation with the zero order with respect to hydroperoxide was defined for the first time.

When oxidation follows the zero order with respect to POOH, the maximum rate of oxygen absorption in the third steady-state stage (v_3) depends on the oxygen pressure and tends to a limit at high P_{O_2} :

$$v_3 \sim \left(\frac{P_{O_2}}{b + P_{O_2}} \right)^{0.5}.$$

Unlike v_3 , the rate v_1 (in the induction period) does not reach a constant value as P_{O_2} increases; according to Eqn (3), $v_1 \rightarrow P_{O_2}^{0.5}$. These differences, which have not been interpreted in terms of the homogeneous model, are explained in the heterophase model by assuming that oxygen acts twice as an initiator of oxidation chains during the induction period — first, in the generation of s-radicals and, second, in the s,v-transfer of the free valence. In the steady-state stage of the process, oxygen no longer acts as the main initiator but still promotes the passage of radicals through the structural ‘bottle-neck’.

3. The mechanism of decomposition of POOH by oxidation products

As has already been noted, the synchronism of the absorption of oxygen and accumulation of the hydroperoxide is violated starting from some point due to the reaction of POOH with reaction products (note that decomposition of POOH in oxidised polyolefin in the absence of oxygen follows a chain mechanism,^{16, 34} as opposed to the non-chain decomposition of POOH during polymer oxidation).

Carboxylic acids are known to accelerate hydroperoxide decomposition.^{3, 44, 45} Study of reactions in mixtures of cumene hydroperoxide with acetophenone, dimethylphenylcarbinol, and benzoic acid showed that only the acid can markedly accelerate hydroperoxide decomposition (giving free radicals).⁴⁵ Acids are among the major products of oxidation of polyolefins; they are characterised by a broad molecular-mass distribution. It should be expected that acids with long molecular tails incorporated in the micellar sponge would not affect much the decomposition of POOH because they cannot freely migrate over the matrix. The decomposition is catalysed, most probably, by the mobile frag-

ment acids formed upon oxidative abstraction of terminal ketone groups.

The equation for the rate of formation of terminal ketones

$$\begin{aligned} v_{\text{CO},t} &= \alpha_t k_4 [\text{E}] [\text{POO}^*] = \alpha_t k_3 [\text{POO}^*] = \\ &= \frac{\gamma_t v_{[\text{POOH}],3}}{(1 + C/[\text{POOH}])^{0.5}} \end{aligned}$$

$[\alpha_t]$ is the yield of $(\text{CO})_t$ and $\gamma_t = \alpha_t k_3 k_2^{-1}$ can be simplified taking into account the fact that the accelerated stage on the curves of absorption of O_2 (and accumulation of CO groups) is substantially shorter than the steady-state stage (see Fig. 2)^{15, 21, 41–43, 46, 47}

$$v_{\text{CO},t} = \gamma_t v_{[\text{POOH}],3} = \text{const},$$

$$[\text{CO}]_t = \gamma_t v_{[\text{POOH}],3} t.$$

Then the rate of the formation of mobile acids (AH) can be written as

$$\frac{d[\text{AH}]}{dt} = k_5 [\text{CO}]_t [\text{POO}^*] = k_5 \gamma_t v_{[\text{POOH}],3} t$$

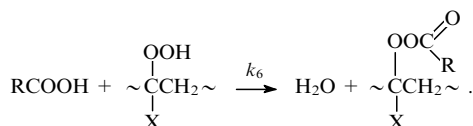
and their amount is equal to

$$[\text{AH}] = B t^2, \quad (14)$$

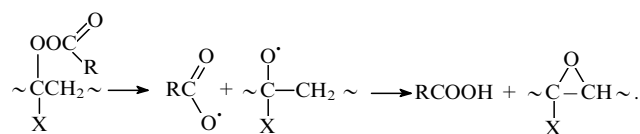
where $B = 0.5 k_5 \gamma_t v_{[\text{POOH}],3} = \text{const}$. Equation (14) is quadratic with respect to time. This accounts for the accelerated accumulation of acids observed at high levels of polyolefin oxidation, despite the substantial decrease in the concentration of POOH after the $[\text{POOH}]_{\text{max}}$ has been attained.^{48, 49}

It should be noted that the consumption of POOH, which accelerates with time, does not influence the invariant rate v_3 of the third macrokinetic stage of autooxidation; this indicates that the yield of radicals in the catalysed reaction is negligibly low.

An adequate scheme of the catalysed process should include condensation of POOH with the acid migrating in the sponge



The peroxy ester thus formed dissociates when the v-nanopore containing it undergoes fluctuation expansion to the volume of an s-nanopore; dissociation gives radicals, which disproportionate with regeneration of the acid without having time to depart from the expanded 'rigid cage'



This scheme is equivalent to the scheme of an intra-cage reaction in which radicals do not migrate to the bulk of the reacting material.¹⁶

Taking account of these considerations, we obtain a fuller kinetic equation for the rate of accumulation of hydroperoxide

$$\frac{d[\text{POOH}]}{dt} = \frac{v_{[\text{POOH}],3}}{(1 + C/[\text{POOH}])^{0.5}} - k_6 [\text{AH}] [\text{POOH}];$$

with allowance for Eqn (14), it acquires the form

$$\frac{d[\text{POOH}]}{dt} = \frac{v_{[\text{POOH}],3}}{(1 + C/[\text{POOH}])^{0.5}} - K [\text{POOH}] t^2, \quad (15)$$

where $K = 0.5 k_6 k_5 \gamma_t v_{[\text{POOH}],3}$, and the rate $v_{[\text{POOH}],3}$ at a saturating pressure of oxygen is

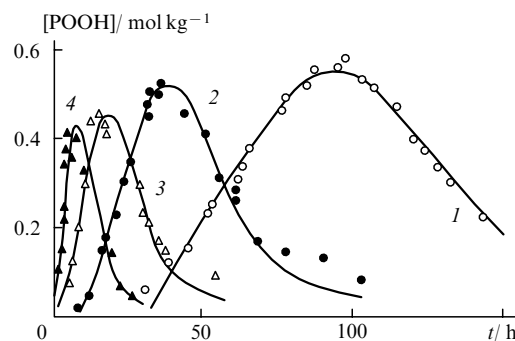


Figure 8. Calculated curves for accumulation of hydroperoxide during the oxidation of APP in air at temperatures of 90 (1), 100 (2), 110 (3) and 120 °C (4) (dots correspond to experimental results from Ref. 50).

$$v_{[\text{POOH}],3} = k_2 \left(\frac{\delta k_{0s} k_{vs} k_m}{4 k_t^f k_t k_{1s}} \right)^{0.5}. \quad (16)$$

The equation describing the rate of oxygen absorption remains the same in the steady-state period [see Eqn (11)]

$$\begin{aligned} v &= k_1 [\text{P}^*] [\text{O}_2] = (k_2 + \eta k_3) [\text{POO}^*] = v_{\text{CO}} + v_{[\text{POOH}],2} = \\ &= \frac{v_3}{(1 + C/[\text{POOH}])^{0.5}} = \frac{v_{[\text{POOH}],3}}{\varphi (1 + C/[\text{POOH}])^{0.5}}, \end{aligned}$$

where η is the multiplicity of oxygen absorption steps in the epoxide branches of oxidation and φ is the yield of POOH after absorption of 1 mol kg⁻¹ of oxygen.

The data obtained using differential kinetic equations (11) and (15) were compared with experimental data on the oxidation of molten APP (Fig. 8),⁵⁰ LDPE (Fig. 9),⁹ ethylene-propylene copolymers (EPC) (Fig. 10),⁵¹ solid-like IPP-1 and IPP-2 films differing in the size of spherulites (Fig. 2),^{24, 31} and home-manufactured polypropylene (IPP-3) (Fig. 11).[†] The theoretical curves presented in Figs 2 and 8–11, were calculated by the Runge–

[†] Data on the oxidation of polypropylene were provided by L N Guseva.

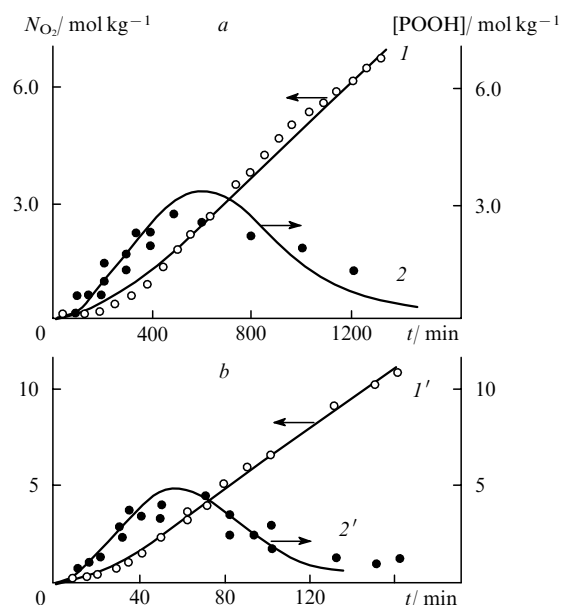


Figure 9. Calculated curves for the absorption of oxygen (I, I') and accumulation of hydroperoxide (2, 2') during oxidation of a LDPE melt at temperatures of 130 (a) and 160 °C (b) and $P_{\text{O}_2} = 100$ kPa (dots correspond to the experimental data from Ref. 9).

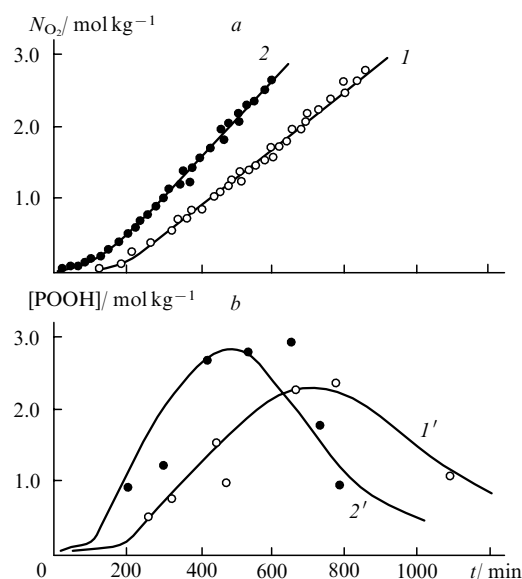


Figure 10. Calculated curves for the absorption of oxygen (*a*) and accumulation of hydroperoxide (*b*) in EPC-1 (*I*, *I'*) and EPC-2 (*2*, *2'*) melts at 130 °C and $P_{O_2} = 40$ kPa (dots correspond to the experimental data from Ref. 51).

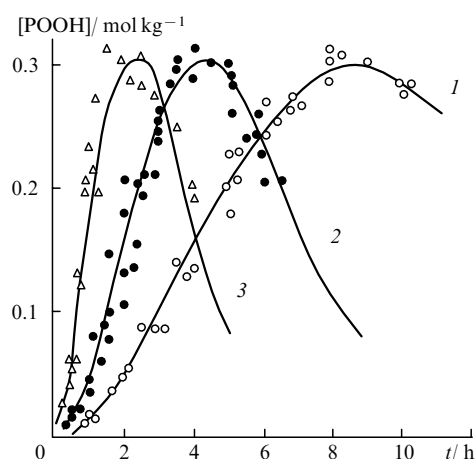


Figure 11. Experimental points and calculated curves for the accumulation of hydroperoxide during oxidation of IPP-3 in air at temperatures of 120 (*I*), 130 (*2*) and 140 °C (*3*).

Kutta method using a simplified version in which Eqns (11) and (15) were integrated separately.⁵² This simplification, used instead of solving the set of two equations, restricts the scope of calculations at high degrees of oxidation by the condition $C/[POOH] < 1$, which is still quite sufficient to perform the given task.

The v_3 and $v_{[POOH],3}$ values were found by drawing tangents to the ascending branches of the curves shown in Figs 2 and 8–11. The coefficients C and K were determined using Eqns (11) and (15). Due to the scatter of experimental points and the values for the induction periods (τ) and the accumulated hydroperoxide concentrations $[POOH]_1$ corresponding to these periods, all the above-listed parameters had to be refined by performing series of calculations in order to attain the best agreement between the calculated curves and experimental points.

The curves for the variation of the concentration of POOH in APP being oxidised in air at temperatures of 90, 100, 110 and 120 °C are presented in Fig. 8.⁵⁰ These curves are matched by the following kinetic characteristics:

$T/^\circ\text{C}$	τ/h	$v_{[POOH],3}/\text{mol kg}^{-1}\text{h}^{-1}$	K/h^{-3}
90	33	0.0129	6.3×10^{-6}
100	10	0.0255	5.6×10^{-5}
110	2	0.0400	3.0×10^{-4}
120	0–1	0.0700	2.0×10^{-3}

In all cases, the equality $C = [POOH]_1 = 0.02$ mol litre⁻¹ holds. The relevant general equations have the following form on the minute time scale

$$\tau = 5.25 \times 10^{-19} \exp(E_\tau/RT) \text{ min},$$

$$v_{[POOH],3} = 2.1 \times 10^6 \exp(-E_{[POOH]}/RT) \text{ mol litre}^{-1} \text{ min}^{-1},$$

$$K = 3.9 \times 10^{22} \exp(-E_K/RT) \text{ min}^{-3},$$

where $E_\tau = 150$, $E_{[POOH]} = 69.5$, $E_K = 230$ kJ mol⁻¹.

Figure 9 presents the calculated curves for the absorption of oxygen and for the accumulation of POOH in a melt of LDPE subjected to oxidation at an oxygen pressure of 100 kPa and temperatures of 130 and 160 °C. These curves are matched by the following kinetic characteristics:

$T/^\circ\text{C}$	τ/min	$v_3/\text{mol kg}^{-1}\text{min}^{-1}$	$v_{[POOH],3}/\text{mol kg}^{-1}\text{min}^{-1}$	K/min^{-3}
130	160	0.006	1.05×10^{-3}	1.7×10^{-8}
160	12	0.076	1.45×10^{-2}	1.6×10^{-5}

The curves for LDPE obtained in another publication⁹ at 150 °C ($P_{O_2} = 100$ kPa), which are not given in Fig. 9, are in good agreement with experimental data for $\tau = 35$ min, $v_3 = 0.036$, $v_{[POOH],3} = 0.005$ mol kg⁻¹ min⁻¹ and $K = 1.0 \times 10^{-6}$ min⁻³. In the case of LDPE, the equality $C = [POOH]_1 = 0.02$ mol kg⁻¹ also holds. The corresponding general equations have the following form:

$$\tau = 4.34 \times 10^{-15} \exp(E_\tau/RT) \text{ min},$$

$$v_3 = 8.86 \times 10^{13} \exp(-E/RT) \text{ mol kg}^{-1} \text{ min}^{-1},$$

$$v_{[POOH],3} = 1.48 \times 10^{13} \exp(-E_{[POOH]}/RT) \text{ mol kg}^{-1} \text{ min}^{-1},$$

$$K = 1.86 \times 10^{31} \exp(-E_K/RT) \text{ min}^{-3},$$

where $E_\tau = 128.4$, $E = 124.4$, $E_{[POOH]} = 124.4$, $E_K = 300$ kJ mol⁻¹. The average yield of hydroperoxide is $\phi = 0.167$.

Figure 10 shows the calculated curves for the absorption of oxygen and accumulation of POOH in the EPC-1 and EPC-2 samples, the macromolecules of which contain 1.5 mass % and 24 mass % of propylene units, respectively.⁵¹ In this case, the results of calculations are in good agreement with experimental data for the following kinetic parameters:

for EPC-1 — $C = [POOH]_1 = 0.01$ mol kg⁻¹, $\tau = 180$ min, $v_3 = 0.004$, $v_{[POOH],3} = 6.2 \times 10^{-4}$ mol kg⁻¹ min⁻¹, $K = 1.0 \times 10^{-8}$ min⁻³, $\phi = 0.15$;

for EPC-2 — $C = [POOH]_1 = 0.02$ mol kg⁻¹, $\tau = 100$ min, $v_3 = 0.005$, $v_{[POOH],3} = 1.1 \times 10^{-3}$ mol kg⁻¹ min⁻¹, $K = 2.8 \times 10^{-8}$ min⁻³, $\phi = 0.22$.

Similar calculated curves for samples of IPP-1 (with small spherulites) and IPP-2 (with large spherulites) subjected to oxidation at 130 °C and $P_{O_2} = 40$ kPa are presented in Fig. 2. Satisfactory agreement between theoretical and experimental results is attained with the following parameters:

for IPP-1 — $C = 0.025$ mol kg⁻¹, $[POOH]_1 = 0.01$ mol kg⁻¹, $\tau = 10$ min, $v_3 = 0.0365$, $v_{[POOH],3} = 0.005$ mol kg⁻¹ min⁻¹, $K = 3.0 \times 10^{-6}$ min⁻³, $\phi = 0.14$;

for IPP-2 — $C = 0.025$ mol kg⁻¹, $[POOH]_1 = 0.01$ mol kg⁻¹, $\tau = 40$ min, $v_3 = 0.022$, $v_{[POOH],3} = 0.004$ mol kg⁻¹ min⁻¹, $K = 1.7 \times 10^{-6}$ min⁻³, $\phi = 0.18$.

The theoretical curves for the accumulation of POOH in IPP-3 samples being oxidised in air (Fig. 11) were constructed for $C = [\text{POOH}]_1 = 0.01 \text{ mol kg}^{-1}$. These curves are matched by the parameters presented below

$T/^\circ\text{C}$	τ/h	$v_{[\text{POOH}]_3}/\text{mol kg}^{-1} \text{ h}^{-1}$	K/h^{-3}
120	1	0.056	0.003
130	0.4	0.115	0.026
140	0	0.190	0.110

The general equations for the parameters τ , $v_{[\text{POOH}]_3}$ and K on the minute time scale have the form

$$\tau = 6.66 \times 10^{-15} \exp(E_\tau/RT) \text{ min},$$

$$v_{[\text{POOH}]_3} = 7.72 \times 10^8 \exp(-E_{[\text{POOH}]/RT}) \text{ mol kg}^{-1} \text{ min}^{-1},$$

$$K = 1.94 \times 10^{23} \exp(-E_K/RT) \text{ min}^{-3},$$

where $E_\tau = 120$, $E_{[\text{POOH}]} = 90$, $E_K = 234 \text{ kJ mol}^{-1}$.

Calculations show that the theoretical equations (11) and (15) for a heterophase process describe correctly the relationship between the curves for the absorption of oxygen and accumulation of POOH and account for their non-synchronism over a long time interval and for the succession of induction and self-acceleration periods and a steady-state period characterised by a constant rate of oxygen absorption. During these periods, the yield of POOH per mole of absorbed oxygen does not change, although the concentration of POOH passes through a maximum. This indicates that the process is mainly due to the reaction of POOH with the accumulating reaction products and that the contribution of the chain reaction of POOH is negligibly small.

Catalytic decomposition of polymeric hydroperoxides is characterised by a high effective activation energy E_K . In accordance with the heterogeneous scheme, the rate of catalytic reaction is determined by the rate of interaction of peroxy radicals with the terminal ketone groups and of the condensation of POOH with acids (the activation energies of these reactions are E_5 and E_6 , respectively). The occurrence of these reactions might require strong thermomechanical fluctuations able to extend a v-nanopore of the micellar sponge to the appropriate size. Thus for a LDPE melt, $E_K = 300 \text{ kJ mol}^{-1}$, i.e. it is greater than the corresponding values for APP and IPP melts in which the activation energies are 230 and 234 kJ mol^{-1} , respectively; this can be due to the more ordered arrangement of the chain segments in LDPE^{32,53} (or to a smaller size of steady-state v-nanopores and greater relative increase in the volume during fluctuation beats).

When the degree of oxidation is high, the theoretical curves for the variation of the concentration of POOH presented in Figs 8–11 can markedly deflect downwards from the experimental points. This can be explained by assuming that the acids (catalysing decomposition of POOH) are lost due to evaporation and to side reactions which are not taken into account in the scheme. Evaporation of monomeric fragments from a polymer being oxidised is limited, unlike the transfer of oxygen,⁵⁴ by physical diffusion at any sample thickness admissible from the experimental standpoint; therefore, the average concentration of volatile acids depends on the thickness of polymer films, which substantially influences $[\text{POOH}]_{\text{max}}$.

It is also noteworthy that experimental curves 3, 4 in Fig. 2 deviate at high degrees of oxidation from the theoretical curves 5, 6 (when the concentration of POOH markedly decreases having passed through a maximum). Among other reasons, this may be due to the distortion of the amount of absorbed oxygen measured by a pressure gauge, caused by the accumulation of gaseous oxidation products, namely, CH_4 , CO and H_2 , which are not absorbed by sorbents meant for H_2O and CO_2 and do not freeze out at the liquid nitrogen temperature. These gases are not only evolved during polymer oxidation but are also formed in the gas-phase oxidation of the volatile oxidation products.

4. Phenomenological consequences

The sequential replacement of macroscopic stages of the reaction is a general feature of the oxidation of high-molecular-mass hydrocarbons (Fig. 12).

The whole set of experimental data presented in Fig. 12 can be described by only one curve, characterised by a rather long self-acceleration period.^{4,27} However, this masks the real patterns of individual curves for each particular polymer. Meanwhile, by distinguishing a series of points for each polymer (see Fig. 12), one can easily make sure that the self-accelerated stage, which follows the induction period, is actually much shorter and is soon replaced by a prolonged steady-state period, which obeys zero-order kinetics with respect to hydroperoxide, i.e. the pattern described above is represented in this case.

The above relation giving the induction period of the oxidation of LDPE [$\tau = 4.34 \times 10^{-15} \exp(128000/RT) \text{ min}$] can be supplemented by two other relations, which were derived from the plots taken from two publications:^{27,55} $\tau = 3.93 \times 10^{-12} \exp(107000/RT) \text{ min}$ (see Ref. 27) and $\tau = 2.5 \times 10^{-9} \exp(85700/RT) \text{ min}$ (Ref. 55). The presence of three different expressions for one polymer (LDPE) implies, on the one hand, that the activation energies E_τ vary over wide limits and, on the other hand, that the pre-exponential factor (τ_0) varies simultaneously with E_τ , i.e. the so-called compensation effect (CEF) is observed.⁶

For each of the above-mentioned polymers, the following relation holds:

$$\ln \frac{1}{\tau_0} = -12.0 + 3.6 \times 10^{-4} E_\tau.$$

The compensation effect is also displayed in the description of the steady-state rates of the accumulation of hydroperoxide in APP, IPP-3 and LDPE (in $\text{mol kg}^{-1} \text{ min}^{-1}$):

$$\text{for APP} — v_{[\text{POOH}]_3} = 2.1 \times 10^6 \exp(-69500/RT),$$

$$\text{for IPP-3} — v_{[\text{POOH}]_3} = 1.93 \times 10^9 \exp(-90000/RT) \text{ (recalculated in relation to the non-crystalline phase of the polymer),}$$

$$\text{for LDPE} — v_{[\text{POOH}]_3} = 1.48 \times 10^{13} \exp(-124700/RT).$$

These formulae can be supplemented by the results of calculations performed using the plots given in the study by Iring *et*

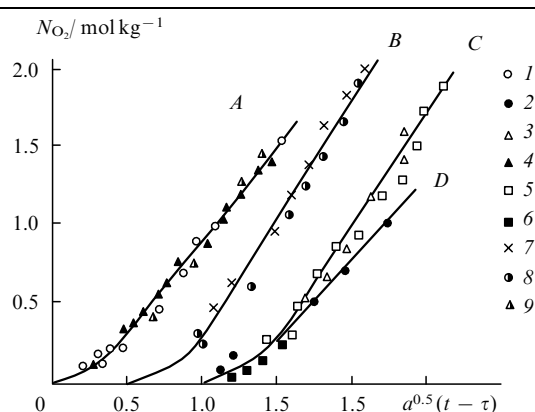


Figure 12. Amount of absorbed oxygen vs. the $a^{0.5}(t - \tau)$ value in the oxidation of several polymers:

(1) polyethylene (90°C); (2) polypropylene (130°C); (3) ethylene copolymer with 13.5% of propylene (130°C); (4) poly-4-methylpent-1-ene (130°C); (5) a vulcanised synthetic rubber (110°C); (6) polystyrene (160°C); (7) polyhept-1-ene (100°C); (8) polynon-1-ene (100°C); (9) epoxy rubber (200°C).^{4,27}

Curves B, C and D are shifted relative to curve A along the abscissa axis by one (B) or two (C, D) scale units (one scale unit is equal to 0.5). The $a^{0.5}$ values, induction periods and oxygen pressures are given in a monograph⁴.

al.⁵⁵ for the oxidation of LDPE (the value $\varphi = 0.17$ found for LDPE was employed in the calculations):

in the region of $T < T_m$,

$$v_{[\text{POOH}]_3} = 1.87 \times 10^6 \exp(-76\,000/RT) \text{ mol kg}^{-1} \text{ min}^{-1},$$

in the region of $T > T_m$

$$v_{[\text{POOH}]_3} = 4.25 \times 10^{15} \exp(-145\,000/RT) \text{ mol kg}^{-1} \text{ min}^{-1},$$

where T_m is the melting point of crystallites.

In this case, the relationship between the $E_{[\text{POOH}]}$ values and the pre-exponential factors ($v_{[\text{POOH}]_3}^0$) is described by a common equation

$$\ln(v_{[\text{POOH}]_3}^0) = -7.0 + 3 \times 10^{-4} E_{[\text{POOH}]},$$

which does not depend on the presence of substituents in macromolecules or on the change in $E_{[\text{POOH}]}$ following the transition of LDPE from the solid-like state to the molten state.

Attention is drawn to a peculiar inversion of the position of APP on the CEF plots; the point corresponding to this polymer is located right at the top of the straight section in the dependence of $\ln(1/\tau_0)$ on E_τ but it moves to the very bottom of the straight section in the dependence of $\ln(v_{[\text{POOH}]_3}^0)$ on $E_{[\text{POOH}]}$. Isotactic polypropylene behaves in a similar way.

The heterophase model of oxidation of polymers is at an early stage of development when structural-kinetic reaction models are tested; it still cannot provide a theoretical interpretation of the presence of CEF. However, even now, it is clear that the widely held opinion that the reaction rate should necessarily increase upon an increase in the molecular-segment mobility of macromolecules is unfounded.

Indeed, the rates of accumulation of the hydroperoxide groups at the third macroscopic stage of oxidation of molten APP and LDPE at 130 °C are 2.0×10^{-3} and 1.0×10^{-3} mol kg⁻¹ min⁻¹, respectively; however, in solid IPP-3, this rate is 4.0×10^{-3} mol kg⁻¹ min⁻¹.

It is noteworthy that, although IPP is oxidised faster than LDPE at 130 and 150 °C, the rate of the rupture of the IPP macromolecules determined by viscometry is 6 times as low.⁴² According to our heterophase scheme, this fact, which had not been interpreted previously,⁴² is associated with the existence of a competing pathway for the decomposition of the polymeric alkoxyl arising in the epoxide oxidation of IPP, accompanied by liberation of a methyl radical. No route of this type exists for LDPE; thus, the internal alkoxyl radicals formed in LDPE are mainly converted with the rupture of macromolecules.

We are reminded that statistical rupture of macromolecules (not related to the elimination of terminal fragments) can also take place in the s-zones of spongy micelles. The contribution of these events to the overall oxidative degradation is rather low due to the low mass fraction of polymeric s-segments. Meanwhile, in some cases, they can determine the physical essence of the process, for example, by ensuring the observance of the first kinetic order with respect to the initiator under conditions of chemically initiated relaxation of stress applied to cross-linked polymers.⁵⁶ The first order with respect to the initiator means that the mechanical strength of polymer samples under the experimental conditions is determined, first of all, by the degree of damage of the continuous three-dimensional paracrystalline framework, *i.e.* by the degree of development of the process that occurs directly in the s-zones of the spongy micelles.²¹

Yet another important remark concerns the coefficient C [see Eqns (9)–(12)], found for the IPP-1 and IPP-2 films ($C = 0.025$ mol kg⁻¹).^{24,31} This coefficient is exactly equal to the constant C determined previously in the experiments on anaerobic decomposition of hydroperoxide in films of previously oxidised IPP-1.³⁴ The point is that decomposition of POOH in this polymer in the absence of oxygen is due to a chain heterophase reaction, whose rate depends not only on the POOH concentration in the v-zones of spongy micelles but also on the POOH

concentration in s-zones and is proportional to $[\text{POOH}]_s^{0.5}$. The initial concentration $[\text{POOH}]_s$ in an anaerobic reaction is determined using Eqn (7); therefore, the constant C characterises both the oxidation and the anaerobic process. Thus, the value $C = 0.025$ mol kg⁻¹ reflects the real relationship between the rates of two heterophase processes which occur in the IPP-1 samples under conditions different in kind, namely, in the absence of oxygen and with active participation of oxygen.

It should be emphasised that the third macroscopic stage of the oxidation of a hydrocarbon polymer is not the last stage because the content of CH and OOH groups in the s-zones should sooner or later substantially decrease. This fact, together with the simultaneous change in the structure of molecular spongy micelles would inevitably produce a situation where Eqn (7) no longer holds and the reaction kinetics have changed. Nevertheless, the heterogeneous-heterophase model appreciably extends the capacities of the kinetic description of the oxidative transformation of hydrocarbon polymers.

V. Oxidation of molten polystyrene

The kinetic curves for the absorption of oxygen and accumulation of POOH in the oxidation of molten polystyrene (PS) (Figs. 13, 14), presented in a publication,⁵⁷ are qualitatively similar to those characterising oxidation of polyolefins. This is quite natural for a carbochain polymer with reactive CH bonds like PS, which is characterised by the same micellar spongy organisation of polymer chains as any non-crystalline polymer.³⁸ Meanwhile, the concentration of the POOH groups formed in PS is 100 times lower (Fig. 14).

Our calculations showed that the experimental data found in the study cited⁵⁷ are adequately described by theoretical equations (11) and (15). Using these equations, the following values were found for the parameters τ , K , and φ

T /°C	τ /h	v_3 /mol kg ⁻¹ h ⁻¹	$10^3 v_{[\text{POOH}]_3}$ /mol kg ⁻¹ h ⁻¹	K /h ⁻³	$10^2 \varphi$
180	0.4	0.06	1.35	0.07	2.25
190	0.05	0.14	2.35	0.44	1.68
200	~0.00	0.30	3.8	2.8	1.27
210	~0.00	0.61	—	—	—

The coefficient C (2.0×10^{-4} mol kg⁻¹) and the concentration of $[\text{POOH}]_1$ (1.5×10^{-4} mol kg⁻¹) are constant in the temperature range of 180–210 °C.

The relevant generalised expressions used to calculate v_3 , $v_{[\text{POOH}]_3}$, and K have the form (on the minute time scale)

$$v_3 = 9.7 \times 10^{12} \exp(-138\,500/RT) \text{ mol kg}^{-1} \text{ min}^{-1},$$

$$v_{[\text{POOH}]_3} = 3.6 \times 10^5 \exp(-88\,300/RT) \text{ mol kg}^{-1} \text{ min}^{-1},$$

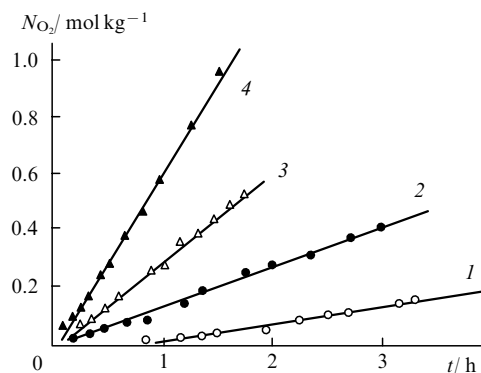


Figure 13. Oxygen absorption during oxidation of a PS melt at 180 (1), 190 (2), 200 (3) and 210 °C (4) and $P_{O_2} = 26.7$ kPa.⁵⁷

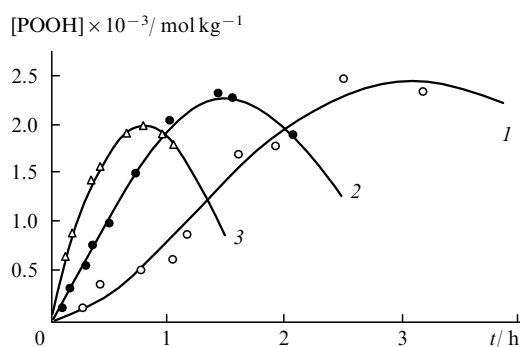


Figure 14. Calculated curves for hydroperoxide accumulation during oxidation of a PS melt at 180 (1), 190 (2) and 200 °C (3) (the dots correspond to experimental data from Ref. 57).

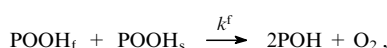
$$K = 7.6 \times 10^{10} \exp(-151\,000/RT) \text{ min}^{-3}.$$

Polystyrene is much less reactive in oxidation than polyolefins. When comparing characteristics of oxidation of PS with the corresponding characteristics of polyolefin oxidation, one can note lower C and $[\text{POOH}]_1$ values.

The low C and hydroperoxide concentrations $[\text{POOH}]_1$ at the end of the induction period are due to high fluctuation mobility of the molecular sponge in a PS melt. This is indicated by the expression $C = k_{0s}k_{-f}(k^f k_f)^{-1}$, the denominator of which is the product of the fluctuation rate constants. In this particular case, it is 100 times as great as that for an LDPE melt. Presumably, the much higher frequency of beats of the nanopores in the PS sponge ensures a higher rate of migration of the OOH groups from the v-zones of spongy micelles to s-zones

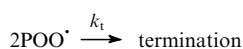


and a higher rate of the radical-free bimolecular reaction,



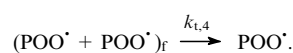
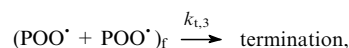
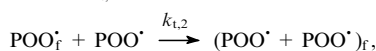
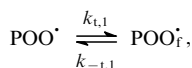
which manifests itself as the fulfillment of Eqns (7), (8), (11) and (13).

In view of the high flickering activity of nanopores in the molecular sponge of PS, a simultaneous increase in the rate of the quadratic termination of reaction v-chains should be expected. However, the notation chosen previously for this step of the oxidation of polyolefins,



does not reflect in an explicit form the influence of the structural factor and formally corresponds to a homogeneous reaction. This simplified approach does not change much the kinetic description of the oxidation of high-molecular-mass polyolefins; however, when considering a wider range of objects, it is necessary to define the chain termination mechanism in more detail.

A more precise scheme of reactions of polymeric peroxy radicals in the molecular sponge should include the steps of fluctuation excitation and deactivation of the nanopores in which the peroxy radicals are located and the step of peroxy migration into a common nanopore and should also reflect the competition between the reaction steps and the departure of the peroxy radicals from the common nanopore



By applying the steady-state concentration condition to fluctuationally excited peroxy radicals and radical pairs, one can easily derive an expression for the chain termination rate

$$v_t = -\frac{d[\text{POO}^\bullet]}{dt} = \frac{2k_{t,1}k_{t,2}k_{t,3}[\text{POO}^\bullet]^2}{(k_{-t,1} + k_{t,2}[\text{POO}^\bullet])(k_{t,3} + k_{t,4})}.$$

When the probability of deactivation of the fluctuationally excited peroxy radicals is high, i.e. $k_{-t,1} > k_{t,2}[\text{POO}^\bullet]$, this expression acquires the form

$$v_t'' = \frac{2k_{t,1}k_{t,2}k_{t,3}}{k_{-t,1}(k_{t,3} + k_{t,4})}[\text{POO}^\bullet]^2 = k_t''[\text{POO}^\bullet]^2, \quad (17)$$

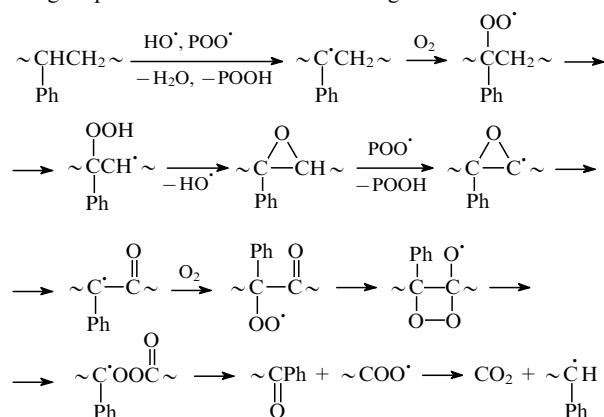
and when the frequency of encounter of two peroxy radicals in one nanopore is high, i.e. $k_{-t,1} < k_{t,2}[\text{POO}^\bullet]$, it has the form

$$v_t' = \frac{2k_{t,1}k_{t,3}}{k_{t,3} + k_{t,4}}[\text{POO}^\bullet] = k_t'[\text{POO}^\bullet]. \quad (18)$$

Although Eqn (17) implies a quadratic dependence of the termination rate on the peroxy radical concentration, it actually refers to a heterogeneous process. Equation (18) describes heterogeneous linear termination of reaction chains, which would be impossible if equivalent peroxy radicals reacted in a homogeneous medium.

The fact that the kinetics of oxidation of PS are described by Eqns (11) and (15) implies the quadratic chain termination in accordance with Eqn (17). Thus, the low rate of oxidation of PS (compared to polyolefins) can be attributed to the great value of the termination rate constant $k_t'' = 2k_{t,1}k_{t,2}k_{t,3}/k_{-t,1}(k_{t,3} + k_{t,4})$; this is due to the fact that the rate constant for the fluctuations ($k_{t,1}$) is high and the rate constant for the 'collapse' of the v-nanopores with an increased size to the initial size ($k_{-t,1}$) is low. The benzene rings present in PS occupy room in nanopores and thus decrease the probability of their 'collapse'. As a consequence, the fluctuation oscillations of the surrounding sponge units become cooperative. The constant $k_{t,2}$ for the capture of the OOH groups by flickering nanopores can increase for the same reason.

The mechanisms of heterophase initiation and termination of reaction chains in the zones of the PS matrix do not change due to the presence of the benzene rings; therefore, expressions (7) and (13) for the steady-state concentrations of peroxy radicals remain valid. The qualitative similarity of the oxidation kinetics of PS and polyolefins implies that the chemical reactions involved in these two processes are the same. In particular, in PS, the terminal ketone groups are formed *via* the following route



In turn, the terminal ketone groups serve as the source of formation of benzaldehyde and benzoic acid (Scheme 3).

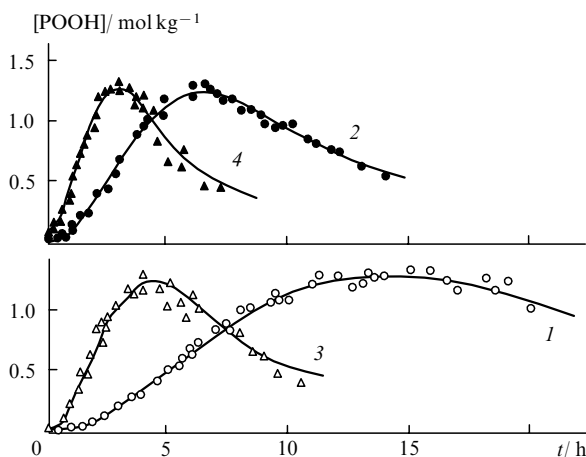
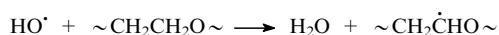
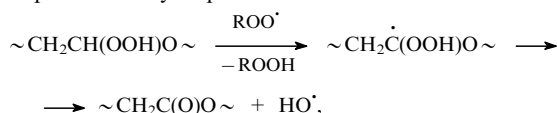


Figure 15. Calculated curves for hydroperoxide accumulation during oxidation of molten PEO in air at 80 (1), 90 (2), 95 (3) and 99 °C (4) (the dots correspond to experimental data from Ref. 18).

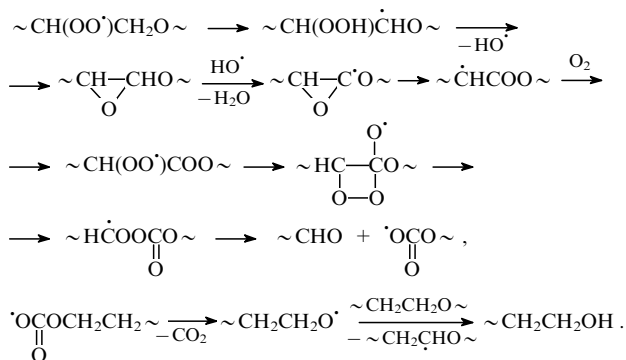
(0.2 mol kg⁻¹ h⁻¹) and ester groups in the polymer (0.35 mol kg⁻¹ h⁻¹). Accumulation of polymeric aldehydes proceeds at a high rate (5 mol kg⁻¹ h⁻¹) without the addition of gas-phase oxygen to macromolecules.

It is worth noting that oxidation of PEO in chlorobenzene and dichlorobenzene (75–95 °C) follows a mechanism of homogeneous chain reaction with the quadratic termination of reaction chains;⁶⁰ this was demonstrated using an initiator — azobisisobutyronitrile. For low degrees of the initiated reaction, the amount of POOH formed coincides almost entirely with the amount of absorbed oxygen. This indicates that the contribution of reactions of alkyl and peroxy macroradicals resulting in the rupture of polymer chains is insignificant.

The initiated oxidation of PEO in solution gives rise to ester groups. The initial rate of formation of these groups is close to zero but it increases to reach a constant value as POOH groups are accumulated.⁶¹ This finding points to the occurrence of induced decomposition of hydroperoxide



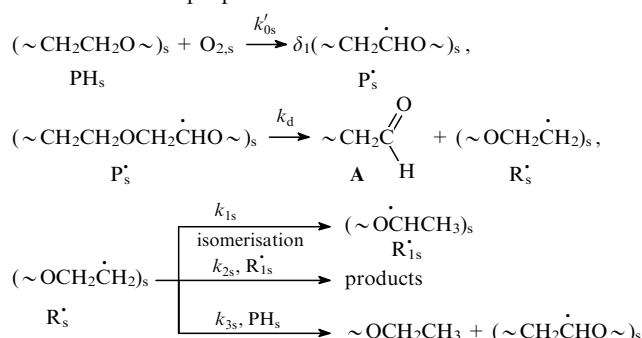
(ROO[•] is a peroxy radical of the initiator). In addition, this means that the probability of α- and β-isomerisation is relatively low. The β-isomerisation steps still do occur, although at a low rate, and thus ensure rupture of internal bonds in macromolecules



We would like to emphasise that the rate of scission of PEO macromolecules in solutions is relatively low and decreases during the reaction.⁶¹

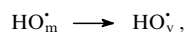
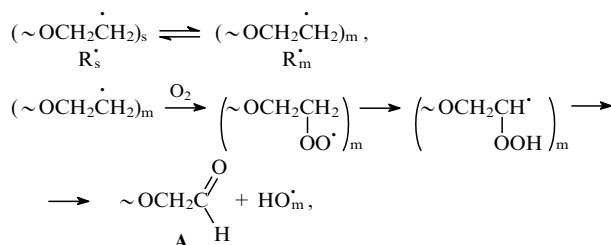
Oxidation of low-molecular-mass molten PEO ($M_n = 6000$), unlike oxidation of PEO in solution, is accompanied, even at high temperature (145 °C), by vigorous formation of water and ester groups (at low concentrations of POOH). Apparently, under these conditions, the macromolecules are not split at the internal bonds.⁶² The same is true for oxidation of molten low-molecular-mass tetraethylene glycol, which is a homologue of PEO.⁶³ The difference between the oxidation processes in solutions and in melts is apparently due to the high concentration of CH₂ groups in the melts and to the predominant role of intermolecular propagation of oxidation chains. The frequency of contacts between macromolecules in solutions of PEO is much lower than in the melts; therefore, the role of intramolecular oxidation increases.

High-molecular-mass molten PEO, unlike the low-molecular-mass homologue, tends to undergo rather vigorous rupture of polymer chains under oxidation conditions. What is significant is that this process does not involve chemical binding of molecular oxygen. This specific feature can be interpreted by assuming that in the melt, long PEO molecules form heterophase spongy micelles, which contain zones with relatively large supernanopores. In these zones, oxygen molecules reside most of the time in the adsorbed state on the pore walls; hence, the alkyl macroradicals formed in the polymer s-segments can react without being oxidised. In view of the foregoing, by analogy with the mechanism of oxidation of polyolefins, the following scheme of reactions in the s-zone can be proposed:

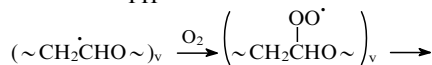
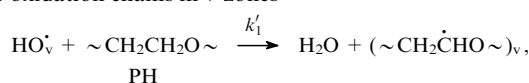


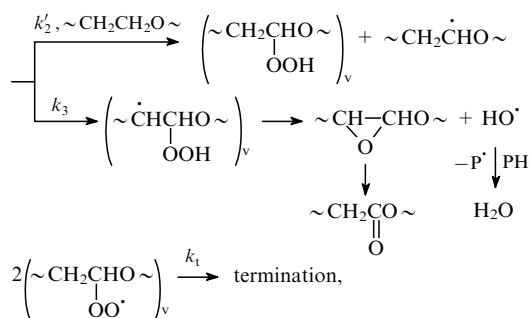
This scheme, unlike that considered above, takes into account the participation of the terminal R_s radicals in the chain propagation steps giving rise to the $\sim\text{CH}_2\dot{\text{C}}\text{HO}\sim$ radicals, which then dissociate to yield aldehydes.

Full scheme of the oxidation process covers also the inter-zone chemical induction

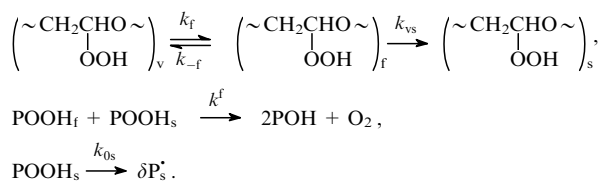


the oxidation chains in v-zones

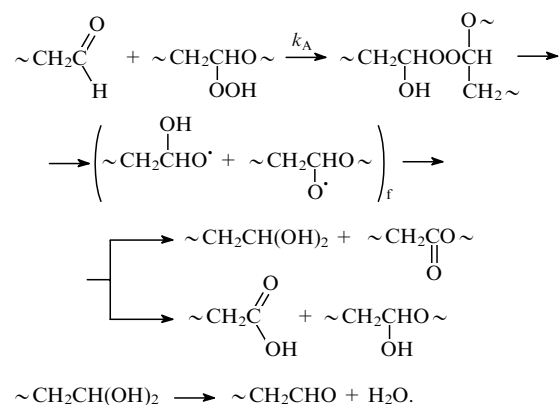




and the steps of occupation of s-zones by hydroperoxide



The main differences between the oxidation mechanisms of PEO and polyolefins are associated with the formation of aldehydes *via* a chain reaction in s-zones and with the decomposition of hydroperoxide *via* the intermediate condensation of aldehydes with POOH considered below



According to this scheme, simultaneously with regeneration of aldehydes, carboxylic acids, which also catalyse decomposition of POOH, can be accumulated in a PEO melt. However, the amount of carboxylic acids is much smaller than that of aldehydes and their role as catalysts must be insignificant.

This heterophase scheme accounts for the existence in the oxidation of PEO of macroscopic induction and self-accelerated periods and a period of steady-state oxidation with a zero order with respect to hydroperoxide. However, the differential kinetic equation describing the variation of the concentration of POOH differs somewhat from the corresponding equation for polyolefins.

By applying the condition of steady-state concentrations to the free radicals appearing in the s-scheme, one can easily derive an expression for the rate of accumulation of aldehydes (A):

$$v_A = \frac{d[A]}{dt} = k_d[P'_s] = \frac{k_{3s}[PH_s]v_i}{2k_{1s}},$$

where v_i is the rate of generation of free radicals in s-zones.

Since the CH bonds are highly reactive, oxidation of PEO soon passes from the induction period to the self-accelerated stage in which the relation

$$v_i = \delta k_{os}[POOH]_s = \frac{\delta k_{os}k_{vs}k_f[POOH]_v}{k_{-f}k_{os} + k_fk_f[POOH]_v}.$$

starts to be obeyed.

Substitution of this relation to the expression for v_A and taking into account that $k_{-f}k_{os} < k_fk_f[POOH]_v$ (the self-accelerated stage is much shorter than the subsequent stages of the process) gives a simplified equation for the rate of accumulation of aldehydes

$$v_A = k_{3s}[PH_s] \frac{\delta k_{os}k_{vs}}{2k_{1s}k_f} = v_{A,3},$$

where $v_{A,3}$ is the maximum constant rate of accumulation of aldehydes in the third stage of oxidation.

The equation for the overall rate of variation of the POOH concentration in the oxidation of PEO has the form

$$\frac{d[POOH]}{dt} = \frac{v_{[POOH],3}}{(1 + C/[POOH])^{0.5}} - k_A[POOH][A], \quad (19)$$

where k_A is the effective rate constant for the condensation. Substitution into relation (19) of the concentration of aldehyde

$$[A] = v_{A,3}t = k_{3s}[PH_s] \frac{\delta k_{os}k_{vs}}{2k_{1s}k_f} t,$$

gives the final equation for the rate of accumulation of POOH

$$\frac{d[POOH]}{dt} = \frac{v_{[POOH],3}}{(1 + C/[POOH])^{0.5}} - K[POOH]t,$$

where

$$K = k_A k_{3s}[PH_s] \frac{\delta k_{os}k_{vs}}{2k_{1s}k_f}. \quad (20)$$

The points determined from the experimental data obtained in Ref. 18 fit well in the integral curves calculated from Eqn (20) using the Runge–Kutta method (Fig. 15). The curves shown in Fig. 15 were constructed using the values $C = 0.08 \text{ mol kg}^{-1}$ and $[POOH]_i = 0.02 \text{ mol kg}^{-1}$ (the concentration of POOH at the end of the induction period) and the following kinetic parameters:

$T/^\circ\text{C}$	τ/h	$v_{[POOH],3}/\text{mol kg}^{-1} \text{ h}^{-1}$	K/h^{-2}
80	1.5	0.184	0.0105
90	0.7	0.40	0.0504
95	0.4	0.60	0.122
99	0.25	0.90	0.263

These parameters match the general formulae of the form

$$\tau = 3.7 \times 10^{-13} \exp(-97400/RT) \text{ min},$$

$$v_{[POOH],3} = 1.0 \times 10^{11} \exp(-91400/RT) \text{ mol kg}^{-1} \text{ min}^{-1},$$

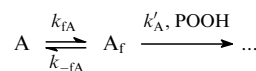
$$K = 1.42 \times 10^{21} \exp(-180600/RT) \text{ min}^{-2}.$$

The experimental dependence of the rate of oxygen absorption v_3 on the pressure of oxygen P_{O_2} at 95°C found by Mikhnev *et al.*¹⁹ is described by the theoretical equation for the heterophase process (see Section IV)

$$v_3 = - \frac{aP_{O_2}^{0.5}}{(b + P_{O_2})^{0.5}},$$

where $a = 0.79 \text{ mol kg}^{-1} \text{ h}^{-1}$, $b = 1.0 \times 10^{-4} \text{ Pa}$.

As regards the mechanism of the catalytic decomposition of POOH, it can be assumed that the terminal aldehyde groups, which differ from internal units by a higher fluctuation mobility, are more efficient in approaching the OOH groups, which are mainly localised in the internal units of macromolecules. In this case, the effective rate constant for the condensation



has the form

$$k_A = \frac{k'_A k_{fA}}{k_{-fA}}, \quad (21)$$

where k_{fA} and k_{-fA} are the frequencies of the fluctuation excitation and deactivation, respectively, of v-nanopores containing aldehyde groups and k'_A is a quasi-elementary constant, which corresponds to the activation energy E'_A .

The activation energy E'_A can be estimated by using the above expression for the constant k_A , appearing in the relation for K . For this purpose, we multiply the numerator and denominator of this expression by k_f and replace k_A by the value from Eqn (21)

$$K = \frac{k'_A k_{fA} k_{3s} [\text{PH}_s] \delta k_{0s} k_{vs} k_f}{2 k_{-fA} k_{1s} k^f k_f}.$$

Let us assume that the reactions with the abstraction of hydrogen atoms (they are characterised by the constants k_{1s} and k_{3s} in the scheme) have virtually equal activation energies ($E_{1s} \approx E_{3s}$). Keeping in mind that the constant C does not depend on the temperature and assuming that the activation energy of the 'collapse' of the excited nanopores is equal to zero ($E_{-f} = E_{-fA} \approx 0$), we obtain the equality $E_{0s} = E^f + E_f$. By examining the expression for the constant K , we can find that the effective activation energy related to K ($E_K = 180.6 \text{ kJ mol}^{-1}$) is the sum

$$E_K = E'_A + E_{fA} + E_{vs} + E_f.$$

Hence,

$$E'_A = 180.6 - E_{fA} - E_{vs} - E_f.$$

Since the fluctuation excitation of nanopores and the migration of OOH groups (with the constants k_f , k_{fA} and k_{vs}) are limited³³ by kinetic jumps of the PEO chain segments and the activation energy of this process is $\sim 40 \text{ kJ mol}^{-1}$, the E'_A value is found to be equal to $\sim 60 \text{ kJ mol}^{-1}$; this fits in the series of values for the effective activation energy of the corresponding liquid-phase transformation.⁶⁴

The results of calculations lead to the following conclusions.

1. The fact that the kinetics of accumulation of POOH in a PEO melt at 80–100 °C are described by the single kinetic equation (20) of the heterophase process indicates that the structure of the micellar framework of s-zones is rapidly restored during oxidation, despite the destruction of s-units of macromolecules to give aldehydes.

2. Poly(ethylene oxide) is oxidised much faster than polypropylene, although the effective activation energies ($E_{[\text{POOH}]}$) in these two cases are close (90 and 91.4 kJ mol^{-1} for IPP-3 and PEO, respectively). This is due to the large difference between the pre-exponential factors in the expressions for the oxidation rate $v_{[\text{POOH}]}$,³ (the corresponding factors are 1.93×10^9 and $1.0 \times 10^{11} \text{ mol kg}^{-1} \text{ min}^{-1}$); in all probability, this is a consequence of the specific features of the heterogeneous mechanism of the oxidation chain termination.

According to Eqn (17), the rate constant for the heterogeneous chain termination k_t comprises several partial structure-mechanical constants, which are directly related to the fluctuation activity of the sponge units in the micellar grains of the polymeric matrix. In the case of PEO, which differs from IPP-3 by the absence of substituents and the presence of a large number of polar ether bonds and, hence, by a high density of intermolecular contacts, restructuring of the sponge during the volume beats of nanopores is apparently hampered. This should either decrease the probability of formation of a pair of peroxy radicals in one nanopore or increase the probability of the escape of peroxy radicals from the intermediate radical pairs.

It should also be emphasised that the activation energy of oxidation of molten PEO is lower than the activation energy of oxidation of a solution of PEO in trichlorobenzene,⁶² which is equal to 147 kJ mol^{-1} . This attests that the molecular-sponge structure, typical of a block polymer, is not formed in solution.

VII. Characteristic features of initiated oxidation of polymers

Initiators are finding extensive practical application in the studies of the kinetics of polymer oxidation. It is believed that they can stabilise for some period the rate of initiation of the transformations (v_{i0}) and thus ensure the non-branching-chain reaction mode. The researchers relying on the theory of homogeneous liquid-phase oxidation often restrict the measurements to the oxygen absorption rate.⁸ By calculations carried out in terms of homogeneous schemes, researchers find the apparent length of the oxidation chains and other kinetic parameters, which allow theoretical construction of the initial sections of kinetic curves for the absorption of oxygen; the results obtained by different authors can be compared more or less successfully.

When oxidation of polymers is treated as a homogeneous process, the scope of the use of the initiation method in kinetic investigations is restricted by several conditions.⁸ In particular, it is required that the initiator be the main source of radicals throughout the experiment (t) {i.e. the condition $v_{i0} > k_i[\text{POOH}]$ should hold}; the admissible working time interval estimated from the inequality $k_i t < 1$ should be $\sim 1000 \text{ s}$. The restrictions imposed on the parameters of initiated processes actually result in a purely formal mathematical description of the short stage of the process. This description is in fact adjusted to the known schemes of homogeneous reactions.

Meanwhile, as shown above, the kinetic features of the polymer process do not fit into the framework of the homogeneous reaction model. In the preceding Sections, we disclosed the mechanism of successive macroscopic stages of oxidation, caused by functioning in polymers of a 'structural-kinetic filter,' restricting the migration of free radicals and hydroperoxide between the structural zones of the matrix. This structural filter is also effective in the case of initiated oxidation of PEO and polyolefins.^{15, 19, 20} This is why the introduction of initiators, which reduce the time it takes to reach the maximum rate of the chain reaction, does not increase the maximum rate; excess initiator is either wasted (Fig. 4, 5) or even decreases the oxidation rate.¹⁹

It should be noted that kinetic features of the initiated oxidation of polymers can be elucidated much more comprehensively by analysing them in terms of heterophase models.

1. Structural filter effects

The presence of a structural filter, restricting transfer of the radicals formed upon decomposition of the initiator, is indicated, for example, by the kinetic curves for the variation of the total concentration of peroxides in IPP samples being oxidised in air at 100 °C in the presence of dibenzoyl peroxide²¹ (see Fig. 5). In the absence of BP, oxidation of IPP at 100 °C has an extended induction period ($\sim 35 \text{ h}$). In the presence of BP, the induction period vanishes; however, dibenzoyl peroxide, which readily dissociates and ensures an appreciably higher rate of initiation in homogeneous solutions than POOH, does not realise in full measure its potential as a source of free radicals. Curves 1 and 2 in Fig. 5 indicate that BP substantially accelerates oxidation of IPP; however, when its content is fairly high, the role of the leading initiator rapidly passes to hydroperoxide, while the BP itself becomes an inefficient ballast.

The unproductive loss of the initiator seems to be due to the 'cage effect,' which is considered in the literature as an analogue of the Franck–Rabinovich homogeneous liquid-phase effect.⁸ However, this approach does not provide interpretation of the curves in Fig. 5. In particular, curve 2 shows that accumulation of POOH proceeds at a constant rate from the very first moment when decomposition of BP has just begun (curve 3).

On the one hand, it can be suggested that only the first, minor portion of the initiator is active in the oxidation of IPP; after this portion has decomposed, the process is initiated only by hydroperoxide. In this case, the main bulk of BP should be located as if inside exceptionally rigid 'cages,' which do not let free radicals

migrate to the bulk of the polymeric matrix. In this case, BP is consumed for no result.

On the other hand, one can suggest with equal success that the free radicals formed from BP migrate to the matrix bulk throughout the whole period of BP decomposition, *i.e.* BP does not lose the initiating activity at the beginning. In this case, the invariance of the rate of POOH accumulation observed from the beginning (curve 2) under conditions of continuous decomposition of BP (curve 3) can be interpreted as pointing to the migration of the free radicals derived from BP from the 'homogeneous liquid-phase cages' to the matrix bulk, which is first insignificant and then permanently increases during the process. It can be easily seen that these two 'cage' models are mutually exclusive.

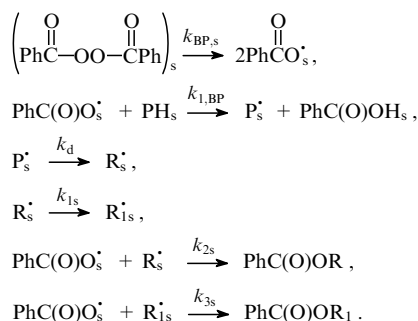
In addition, the homogeneous model of oxidation does not answer the following questions: why does the rate of accumulation of POOH at a relatively high initial concentration of BP (curve 2) remain constant even when BP has completely decomposed? and why do the rates of accumulation of POOH corresponding to the straight sections of curves 1, 2 remain equal and not increase as its concentration grows?

Such 'abnormal features' of the kinetic curves shown in Fig. 5 can be interpreted within the framework of the model of coupled heterophase s- and v-reaction chains. It should be borne in mind that the initiator molecules decompose mainly in the s-zones of the molecular spongy micelles,^{16, 38, 65} into which they get *via* inter-zone exchange. The BP concentration in the s-zones is

$$c_s = \frac{K_e c}{\beta},$$

where K_e is the equilibrium constant for the migration of BP molecules between the zones, c is the overall BP concentration calculated for the whole sample, and β is the fraction of non-crystalline polymeric phase.

When the polymer contains no POOH in the beginning of the process, the following reactions proceed in the s-zone:



According to this scheme, half the BP radicals add to polypropylene macromolecules to give the compounds PhC(O)OR and PhC(O)OR_1 .⁶⁵

Thus, the concentration of the $\text{R}_s^{\bullet}$ radicals

$$[\text{R}_s^{\bullet}] = \frac{k_{BP,s} c_s}{(k_{1s} + k_{2s} k_{BP,s} c_s / k_{1,BP})},$$

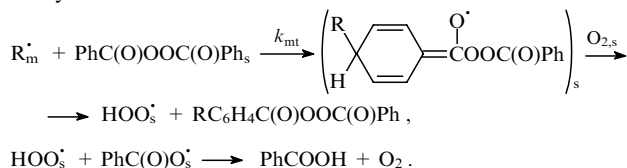
responsible for the induction of the oxidation chains in v-zones, increases as the BP concentration in the polymer grows and at high concentration c , it reaches a limiting value,

$$[\text{R}_s^{\bullet}]_{\text{lim}} = \frac{k_{1,BP}}{k_{2s}}.$$

For this reason, the rate of initiation of the oxidation chains in v-zones also reaches a limiting value for a high concentration of BP; therefore, the 'bottle-neck' effect manifests itself quite clearly in the inter-zone transfer of free valence as the unproductive loss of a great amount of the initiator.

The radical s,v-translation steps are known to be related to the oscillations of the terminal $\text{R}_s^{\bullet}$ radicals between the framework s-domains and the nanopore cavities. In the absence of BP, the

s,v-transfer is due to the interaction of the $\text{R}_m^{\bullet}$ radicals with oxygen (see Section IV). However, the $\text{R}_m^{\bullet}$ radicals are highly reactive towards the benzene rings of BP.^{16, 38, 65} The σ -complexes formed in this reaction are readily oxidised with oxygen with the evolution of free hydroperoxyl radicals $\text{HOO}^{\bullet}$, which participate in the decay of s-radicals



Thus, when no POOH is initially present and the content of BP in the polymer is high, one should expect that not only the limiting rate of the inter-zone chemical induction would be attained but also that the oxidation rate would diminish due to the competing trapping of free valences by dibenzoyl peroxide during the s,v-transfer (in the 'bottle-neck').

In view of the above consideration and with allowance for the scheme of oxidation v-chains, considered in Section IV, we obtain the following expressions for the initial rates of the initiated hydroperoxide accumulation ($v_{[\text{POOH}],BP}$) and oxygen absorption (v_{BP}):

$$\begin{aligned} v_{[\text{POOH}],BP} &= k_2 [\text{POO}^{\bullet}] = k_2 \left(\frac{v_{tr,BP}}{k_t'} \right)^{0.5}, \\ v_{BP} &= (k_2 + \eta k_3) [\text{POO}^{\bullet}] = \frac{k_2 v_{tr,BP}}{\phi k_t'^{0.5}}, \end{aligned}$$

where

$$v_{tr,BP} = k_{tr} [\text{R}_m^{\bullet}] [\text{O}_{2,s}] = \frac{k_m k_{BP,s} c_s P_{O_2}}{(b + b_1 c_s + P_{O_2})(k_{1s} + b_2 c_s)} \quad (22)$$

[$b_1 = k_m(\gamma_s k_{tr})^{-1}$, $b_2 = k_{2s} k_{BP,s} k_{1,BP}^{-1}$]. Equation (22) implies that the relation

$$v_{BP} \sim \frac{v_{tr,BP}^{0.5}}{k_t'^{0.5}} \sim (k_i c)^{0.5},$$

where $k_i = k_{BP,s} K_e \beta^{-1}$, should hold at a relatively low BP concentration in the polymer. It actually does hold, as has been confirmed experimentally. The relation $v_{BP} \sim (k_i c)^{0.5}$ is usually discussed in terms of homogeneous reaction schemes,⁸ although it basically refers to a special case of a heterophase process.

It follows from Eqn (22) that, at low concentrations of the initiator (c_s), the initial rate of oxygen absorption v_{BP} should increase with an increase in pressure P_{O_2} as long as the condition $(b + b_1 c_s) \leq P_{O_2}$ is fulfilled and until the limiting value $v_{BP,lim}$ is attained. As the BP concentration increases, the pattern of the curve $v_{BP} = f(P_{O_2})$ should change in a fairly complex manner. Over some range of the initiator concentration c , the limiting rate $v_{BP,lim}$ would increase but, simultaneously, the range of variation of v_{BP} in the pressure range from 0 to $P_{O_2,lim}$ would become wider. The oxidation of polypropylene at relatively low concentrations of BP has displayed exactly this type of behaviour.^{8, 66} In addition, when the BP concentration is very high, even a decrease in $v_{BP,lim}$ can be expected in conformity with Eqn (22).

Note that the logic of reasoning accepted in the studies by Denisov^{8, 66} was based on the homogeneous reaction model; the observed transformation of the curves for the variation of the oxidation rate *vs.* pressure of O_2 was explained by the existence of diffusion restrictions on the absorption of oxygen. Meanwhile, the heterophase model treats this fact as being due to the 'bottle-neck' effect, which exists even in the absence of diffusion restrictions.

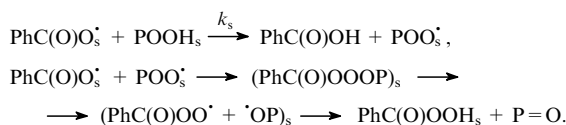
A method for determining kinetic parameters of the processes discussed here borrowed from the homogeneous oxidation practice has been described in a monograph;⁸ this is the method of mixed initiation, which assumes the additivity of the rates of reactions initiated by the hydroperoxide and by an admixed initiator. Within the framework of the heterogeneous scheme, the overall rate of the process can be represented as the sum of the

rates of transfer of free valences through the structural 'bottle-neck', $v_{\Sigma} \sim (v_{tr,BP} + v_{tr,2})^{0.5}$. The kinetics of the oxygen absorption would formally comply with the laws of a homogeneous reaction. However, this additivity is often disturbed because POOH groups react with the initiator in the s-zones of the spongy micelles. The mechanisms of these reactions and the specific features of the kinetics of the initiated oxidation of polymers brought about by these reactions are considered below.

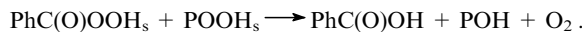
2. Suppression of the initiator by the hydroperoxide

We have considered above the decrease in the initiation efficiency according to the 'self-locking' mechanism at relatively high initiator (BP) concentrations. This mechanism implies capture of the $R_s^{\bullet}$ radicals, responsible for the inter-zone chemical induction, by the primary $PhC(O)O_s^{\bullet}$ radicals and by the dibenzoyl peroxide itself. However, this does not exhaust the specific features of the initiated process. Indeed, it can be seen from Fig. 5 (curve 2) that the oxidation rate in the presence of a high concentration of BP not only reaches the maximum possible value at the very beginning but also does not change subsequently during decomposition of BP and accumulation of POOH. In other words, POOH soon becomes the main initiator (note that the role of the hydroperoxide in restricting the initiator efficiency can also be clearly followed in experiments with initiators that dissociate with difficulty^{15, 19, 21}).

After POOH groups have appeared in the s-zones, in addition to the reactions described above (see Section VII.1), trapping of the initiator free radicals by hydroperoxide occurs followed by recombination and disproportionation steps



Peroxobenzoic acid reacts with hydroperoxide giving no free radicals



Taking into account the schemes for the s,v-transfer of radicals and for the oxidation chains in the v-zones and the steps of hydroperoxide migration and transformations, the rate of oxygen absorption can be expressed as follows:

$$v_{\Sigma} = (k_2 + \eta k_3)[POO^{\bullet}] = \frac{k_2}{\varphi} \left(\frac{v_{tr,\Sigma}}{k_t''} \right)^{0.5},$$

where the value

$$\begin{aligned} v_{tr,\Sigma} &= \frac{k_m P_{O_2}}{k_{1s}(b + P_{O_2})} \left(\frac{k_{1,BP} k_{BP,s} c_s}{k_{1,BP} + k_s [POOH]_s} + \delta k_{0s} [POOH]_s \right) = \\ &= k_t'' [POO^{\bullet}]^2 \end{aligned} \quad (23)$$

corresponds to the condition of a low concentration of BP ($b_1 c_s < b$, $b_2 c_s < k_{1s}$).

At the very beginning of oxidation when $[POOH]_s$ is close to zero and the relations $k_{1,BP} > k_s [POOH]_s$ and $k_{BP,s} c_s > \delta k_{0s} [POOH]_s$ are obeyed, Eqn (23) becomes simpler and assumes the form

$$v_{tr,BP} = \frac{k_m P_{O_2} k_{BP,s} c_s}{(b + P_{O_2}) k_{1s}} = k_t'' [POO^{\bullet}]^2,$$

and the rate of oxygen absorption is determined by the equation

$$v_{BP} = A(k_{BP,s} c_s)^{0.5} \sim (k_1 c)^{0.5},$$

where

$$A = \frac{k_2}{\varphi} \left[\frac{k_m P_{O_2}}{(b + P_{O_2}) k_{1s} k_t''} \right]^{0.5}.$$

This equation is consistent with the experimental data obtained with relatively low rates of decomposition of the initiator.^{8, 19}

Having occupied s-zones, the hydroperoxide becomes the main initiator. Since benzoyloxy radicals detach hydrogen from the OOH groups hundreds times as fast as from the CH groups,¹⁶ which ensures the fulfillment of the inequality $k_{1,BP}(k_s [POOH]_s)^{-1} \ll 1$, Eqn (23) can be transformed to the form

$$v_{tr,\Sigma} = \frac{k_m P_{O_2} \delta k_{0s} [POOH]_s}{k_{1s}(b + P_{O_2})}.$$

Thus, the oxidation rate is described by the relation

$$v_{\Sigma} = A(\delta k_{0s} [POOH]_s)^{0.5}. \quad (24)$$

To determine the concentration $[POOH]_s$, which appears in Eqn (24), the above reactions involving POOH need to be supplemented by the reactions of the proper transformations of the hydroperoxide (see Section IV.2). This gives the expression

$$[POOH]_s = \frac{k_{vf} [POOH]}{k_{0s} + k^{ff} [POOH] + 2k_s k_{BP,s} c_s / (k_{1,BP} + k_s [POOH]_s)},$$

which can be simplified. An identical transformation with the assumption that $k_{1,BP} \ll k_s [POOH]_s$ (this means that the hydroperoxide located in s-zones traps almost all radicals of the admixed initiator) gives

$$[POOH]_s = \frac{k_{vf} [POOH] - 2k_{BP,s} c_s}{k_{0s} + k^{ff} [POOH]}.$$

Here k_{vf} and k^{ff} are constants corresponding to the $POOH_v \longrightarrow POOH_s$ transfer and the $POOH_v + POOH_s$ reaction, respectively (accomplished through an excited v-nanopore; the detailed mechanism is described in Section IV.2), $[POOH] \approx \beta [POOH]_v$.

By substituting the concentration $[POOH]_s$ into Eqn (24), one can determine the rate of the oxygen absorption in the stage in which two sources of free radicals are effective

$$v_{\Sigma} = A \left(\delta k_{0s} \frac{k_{vf} [POOH] - 2k_{BP,s} c_s}{k_{0s} + k^{ff} [POOH]} \right)^{0.5}.$$

It follows from the above relation that, during the accumulation of the hydroperoxide, the oxidation rate increases to a certain limit, which is attained when $k_{0s} < k^{ff} [POOH]$

$$v_{max} = A \left(\delta k_{0s} \frac{k_{vf} [POOH] - 2k_{BP,s} c_s}{k^{ff} [POOH]} \right)^{0.5}. \quad (25)$$

If the subtrahend in Eqn (25) is sufficiently small, the reaction acquires the zero order with respect to both the initiator and hydroperoxide. Then

$$v_{max} = A \left(\frac{\delta k_{0s} k_{vf}}{k^{ff}} \right)^{0.5}.$$

This conclusion has been confirmed experimentally.^{15, 19, 21}

If the subtrahend in Eqn (25) is great, which is the case for a relatively high rate of dissociation of the initiator ($k_{BP,s} c_s \sim k_i c$), this term makes a contribution to the decrease in the steady-state oxidation rate. This has been observed in experiments with samples of readily oxidisable PEO; an increase in the BP concentration from 0.12 to 0.38 mol kg⁻¹ decreases the oxygen absorption rate by a factor of 1.4.¹⁹ This outcome appears as a paradox but it has a clear physical meaning in terms of the heterophase scheme, pointing to the interaction between two sources of free radicals, which is unproductive for oxidation.

In the scheme that we propose, the formation of peroxobenzoic acid in disproportionation steps and the radical-free reaction of peroxobenzoic acid with POOH can be classified as unproductive consumption of radicals. The possibility of radical-free bimolecular decomposition of peroxobenzoic acid can also be

assumed, by analogy with the heterogeneous reaction $\text{POOH}_f + \text{POOH}_s$ or, for example, with the known decomposition of *tert*-butyl hydroperoxide⁶⁷ and aromatic dihydroperoxide⁶⁸ in liquid solutions.

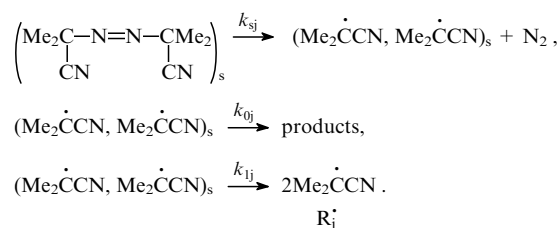
In this connection, the known fact of retardation of the initiated oxidation of polypropylene and polyethylene by the addition of cumene hydroperoxide⁸ (with BP as the initiator) can be considered from a new standpoint. In all probability, this fact is due to the decrease in the rate of initiation ($v_{tr,\Sigma}$) of oxidation v -chains caused by the unproductive loss of the radicals generated in s -zones. Anyway, the idea of acceleration of the oxidation chain termination upon the involvement of mobile cumene peroxy radicals⁸ does not seem quite convincing because the rate of injection of free valences into v -zones is extremely low. In our opinion, the conditions in s -zones are much more favourable for trapping of the BP free radicals by the admixed cumene hydroperoxide molecules and for unproductive (with respect to the oxidation chains) interaction between these components.

3. Synergism of the action of hydroperoxide and an initiator

In some cases, the hydroperoxide accumulated in the polymer enhances the efficiency of an admixed initiator. This is indicated by the fact that hydroperoxide has a promotory influence on azobisisobutyronitrile (AIBN),⁶⁹ although the researchers themselves did not interpret this effect. It was found that the rate of oxygen absorption by solid IPP at 82 °C in the presence of 7.5×10^{-2} mol kg⁻¹ of AIBN increases from the very beginning until it reaches a constant level, 4 to 7 times as high as the initial level. This increase is at variance with the view⁸ that the oxidation rate always remains constant as long as the initiation rate is constant. Meanwhile, the rate of oxidation of pre-oxidised IPP samples containing 5×10^{-3} mol kg⁻¹ of POOH and 7.5×10^{-2} mol kg⁻¹ of AIBN is equal from the beginning to the steady-state rate of oxidation of non-oxidised IPP.

The rates of radical generation upon dissociation of POOH and AIBN, found by the inhibitor method (based on the consumption of stable nitroxides) are 7.5×10^{-9} and 7.5×10^{-7} mol kg⁻¹ s⁻¹, respectively. Proceeding from these values and relying on the homogeneous reaction model, the researchers⁶⁹ concluded that AIBN is responsible for the initiation virtually alone, whereas the hydroperoxide ensures branching of the oxidation chains and efficiently decreases the rate constant for the termination of these chains by increasing their length. The last-mentioned conclusion was criticised in a monograph by Popov *et al.*,⁵ who proved that the rate constant for the termination of oxidation chains in IPP does not depend on the content of POOH. This result is confirmed, in particular, by the fact that the radiation-induced oxidation of IPP proceeds at a constant rate. When other initiators are employed (for example, BP and dicumene peroxide), no noticeable change in the rate constant for chain termination upon accumulation of POOH has been identified either.⁸

The discussion around the 'AIBN effect'^{5,8} precluded elucidation of its mechanism because the effect was discussed within the framework of the homogeneous model, which is not valid for this particular case. However, if the mechanism of AIBN initiation is considered in terms of the heterophase model, two initiation rates should be distinguished: (1) the rate of generation of free radicals found by the inhibitor method and corresponding to the process localised in the s -zones of the micellar sponge and (2) the much lower rate of initiation (and termination) of the proper oxidation chains which are continued in v -zones. In this case, the essence of the AIBN effect in question can be explained as follows. Azobisisobutyronitrile decomposes in the s -zones of spongy micelles and generates alkyl cyanoisopropyl radicals, $R_j^\bullet$, which readily react with nitroxides but virtually do not react with macromolecules. The primary $R_j^\bullet$ radicals partially decay without leaving a radical pair, while some of the radicals are oxidised to give reactive peroxy radicals, which do react with macroradicals.

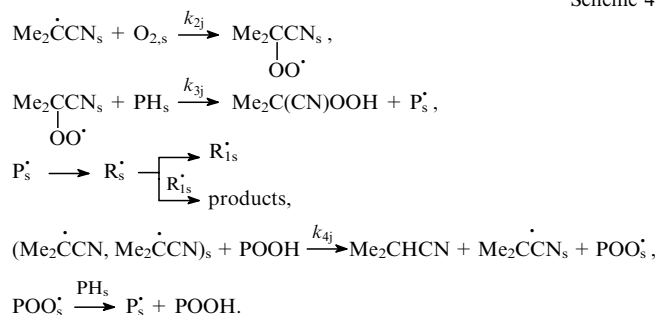


In accordance with the experimental data, the ratio of the rate of formation of the $R_j^\bullet$ radicals to the rate of AIBN decomposition in the IPP matrix at 82 °C amounts to $2k_{ij}/(k_{oj} + k_{ij}) = 0.054$.⁸ Thus, a substantial portion of AIBN radicals decay at the beginning of the process and do not participate in the oxidation.

The situation changes as POOH groups are accumulated in s -zones. Since alkyl radicals are highly reactive towards the abstraction of hydrogen from the OOH groups,^{70,71} they provide an additional opportunity for the formation of the terminal $R_s^\bullet$ macroradicals, which are responsible for the transfer of free valences to the v -zones. In this case, all the generated $R_j^\bullet$ radicals are consumed for the oxidation reaction and thus ensure a hundred percent initiating efficiency of AIBN.

The above considerations can be summarised by the following simplified scheme of transformations (Scheme 4):

Scheme 4



Here we neglect the contribution of POOH to the generation of free radicals, in compliance with the results obtained by the inhibitor method.⁶⁹

According to Scheme 4, the quasi-steady-state concentration of the $[R_s^\bullet]$ radicals, responsible for the chemical s,v -induction,

$$[R_s^\bullet] = \frac{2k_{sj}c_j(k_{1j} + k_{4j}[\text{POOH}]_s)}{k_{1s}(k_{oj} + k_{1j} + k_{4j}[\text{POOH}]_s)}$$

(c_j is the concentration of AIBN in s -zones) increases during the accumulation of POOH from the initial value

$$[R_s^\bullet]_0 = \frac{2k_{1j}k_{sj}c_j}{k_{1s}(k_{oj} + k_{1j})} \text{ for } k_{4j}[\text{POOH}]_s \ll k_{1j}$$

to the limiting value

$$[R_s^\bullet]_{\text{lim}} = \frac{2k_{sj}c_j}{k_{1s}} \text{ for } k_{4j}[\text{POOH}]_s \gg (k_{oj} + k_{1j}).$$

Under these conditions, the rate of oxygen absorption

$$v = \frac{k_2[\text{POO}^\bullet]}{\varphi} = \frac{k_2}{\varphi} \left(\frac{v_{tr}}{k_t'} \right)^{0.5}$$

increases from the initial value v_0 to the limiting value v_{lim} in conformity with the equation

$$\frac{v_{\text{lim}}}{v_0} = \left(\frac{v_{tr,\text{lim}}}{v_{tr,0}} \right)^{0.5} = \left(\frac{[R_s^\bullet]_{\text{lim}}}{[R_s^\bullet]_0} \right)^{0.5} = \left(\frac{k_{oj} + k_{1j}}{k_{1j}} \right)^{0.5}.$$

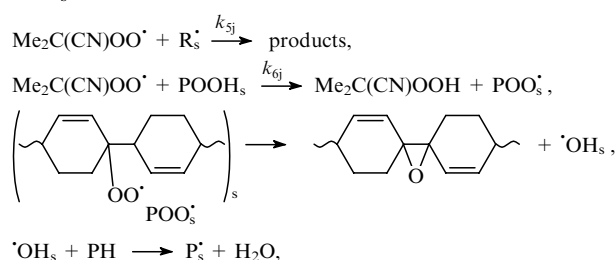
Substitution into this equation of the $k_{1j}(k_{oj} + k_{1j})^{-1} \approx 0.027$ determined experimentally⁸ gives the equality $v_{\text{lim}} = 6v_0$, which is consistent with the value found in another study.⁶⁹

Thus, within the framework of the heterophase reaction model, the specific kinetic feature observed in the initial stage of oxidation of polymers in the presence of AIBN is interpreted as being due to the increase in the initiating efficiency of AIBN,

This means that the main reaction involving free radicals in the oxidation of non-crystalline PCH is abstraction of hydrogen atoms giving rise to allyl type radicals. The subsequent transformations of these radicals in the s- and v-zones of the PCH matrix differ in kind. Indeed, due to the substantial steric restrictions hampering opening of the six-membered carbon rings and epoxidation in narrow v-zones, an intermolecular mechanism of the propagation of oxidation chains comes to the fore.



Now we return to the s-scheme of reactions involving AIBN (see Scheme 4), eliminate the reaction of radical pairs with the hydroperoxide POOH (k_{4j}) (which is unlikely in a vitreous polymer), add reactions involving the $Me_2C(CN)OO^*$, POO^*_s and $\cdot OH_s$ radicals



and write the algebraic condition for the steady-state concentrations of radicals participating in the inter-zone s,v-chemical induction,

$$\begin{aligned} \frac{d[R_s^*]}{dt} &= k_{3j}[Me_2C(CN)OO^*][PH_s] \\ &+ k_{6j}[Me_2C(CN)OO^*][POOH_s] \\ &- k_{5j}[Me_2C(CN)OO^*][R_s^*] = 0. \end{aligned}$$

By solving this equation, we make sure that the concentration

$$[R_s^*] = \frac{k_{3j}[PH_s] + k_{6j}[POOH_s]}{k_{5j}}$$

does not depend on the concentration of the initiator.

The s-scheme for the reactions involving LP is qualitatively the same.

Now we employ the scheme of the s,v-translation of free valences, which is similar in kind to the corresponding scheme for polyolefins, and express the balance of the rates of initiation and termination of oxidation v-chains by the equation

$$v_{tr} = \frac{k_m P_{O_2} [R_s^*]}{b + P_{O_2}} = k_t'' [POO^*]^2,$$

and the rate of oxygen absorption by the equation

$$\begin{aligned} v_1 &= \frac{k_2 [POO^*]}{\varphi} = \\ &= \frac{k_2}{\varphi} \left(\frac{P_{O_2}}{b + P_{O_2}} \right)^{0.5} \left(\frac{k_m k_{3j} [PH_s] + k_m k_{6j} [POOH_s]}{k_{5j} k_t''} \right)^{0.5}. \end{aligned}$$

It can be seen from the latter equation that v_1 does not depend on the concentration of an admixed initiator.

In the absence of an admixed initiator, the steady-state rate of the absorption of oxygen by PCH does not depend on the content of POOH either [Eqn (9)]

$$v_3 = \frac{k_2}{\varphi} \left(\frac{P_{O_2}}{b + P_{O_2}} \right)^{0.5} \left(\frac{\delta k_{0s} k_m k_{vs}}{2 k_t'' k_{1s} k_t''} \right)^{0.5},$$

and the relatively low value of this rate is stipulated by the small value of the product $\delta k_{0s} k_{vs}$.

It is worth noting that, in accordance with the mechanism in question, the constant values of $[R_s^*]$ and v_1 correspond to a relatively high content of the initiator, which provides the 'self-locking' effect in the passage of free valences through the 'bottle-

neck'. It is evident that at low concentrations of the initiator, the 'self-locking' condition is not met; however it is met in the range of AIBN and PL concentrations studied by Chaplanova *et al.*^{72–74} In terms of this mechanism, the dissimilarity between the v_1 values observed in the AIBN- and LP-involving processes is due to the different values of the complex constant

$$\frac{k_{3j}[PH_s] + k_{6j}[POOH_s]}{k_{5j}},$$

characterising the reactions of peroxy radicals derived from AIBN and LP with the CH bonds of the oxidised PCH (POOH) and the macroradicals R_s^* . According to experimental data, this complex constant is greater for the LP radicals.

Thus, the heterophase reaction model interprets the initiated 'jumps' in the oxygen absorption rate, observed in the oxidation of PCH samples, without violating the logical link between this partial model and those describing oxidation of other polymers.

VIII. The model of oxidation of thermofluctuationally active objects

In the preceding Sections, we considered oxidation processes that occur in the mode of heterophase injection of free valences from the zones in which they are generated to the zones in which chain reaction of macroradicals with oxygen takes place. This mode is typical of specimens with relatively low molecular-segment mobility.

Meanwhile, the mobility of units of the molecular sponge can increase appreciably under certain conditions. This is accompanied by an increase in the frequency of formation of fluctuationally excited nanopores (f-nanopores) directly in the grains of spongy micelles. These conditions are fulfilled, for example, in polymers with relatively low molecular masses and, correspondingly, with low macroscopic viscosity (for example, for low-molecular-mass APP) and in a polymer matrix in the state of thixotropic excitation, caused by structural and mechanical relaxation (for example, in oriented IPP).²⁶

Due to excitation in a dynamically active molecular sponge, f-nanopores reach the size of s-nanopores and their lifetime increases because relaxation requires spatial redistribution of numerous units of the sponge in the vicinity of the f-nanopore formed. Since the frequency of formation of f-nanopores is relatively high, they increase the rate of dissociation of the POOH groups in the v-zones of spongy micelles¹⁶ and also trigger off the mechanism of quasi-linear termination of reaction chains according to Eqn (18).

The new steps of initiation and termination of oxidation chains, which are added to the heterogeneous initiation and quadratic termination steps or even prevail in the oxidation, should necessarily change qualitatively the reaction kinetics.

The kinetics of oxidation of low-molecular-mass APP and oriented IPP provide an example of such a change (see Fig. 6). This process displays a fairly prolonged exponential increase in the amounts of oxygen absorbed (curves 1, 3) and the POOH formed (curves 2, 4).²⁶ The amount of oxygen absorbed in the exponential stage reaches 1.5–2.0 mol kg^{−1}, which markedly differentiates this process from the oxidation of high-molecular-mass polyolefins, which includes a short-term 'parabolic' self-accelerated stage and, after 0.1–0.2 mol kg^{−1} of oxygen has been absorbed, switches to the mode characterised by zero-order kinetics with respect to hydroperoxide.

The long-term exponential acceleration of the reaction has also been found in experiments with a model analogue of polyolefins, cetane (oxidation was carried out with the removal of the resulting aqueous phase containing acidic products),⁴⁴ and in experiments with low-molecular-mass APP ($M_n = 2250$) in the temperature range of 120–160 °C⁷⁵ (Fig. 16).

The change in the kinetics of the absorption of oxygen upon orientational drawing has been observed in experiments with IPP (Fig. 6), polyethylene and polymethylpentene films (Fig. 17).^{5, 76}

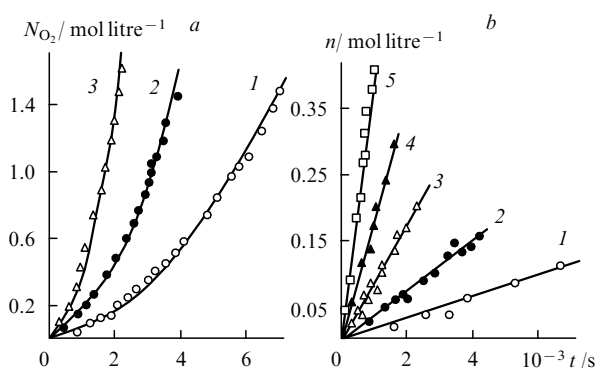


Figure 16. Variation of the amount of oxygen absorbed (*a*) and the number of breaks in macromolecules (*b*)⁷⁵ during oxidation of molten APP ($M_n = 2250$) at an oxygen pressure of 97.3 kPa and temperatures of 120 (1), 130 (2), 140 (3), 150 (4) and 160 °C (5) (the dots correspond to experimental data from Ref. 75).

It can be clearly seen in Fig. 17 how curve 1 for isotropic films (with short self-acceleration and then zero-order kinetics with respect to POOH) is replaced upon film drawing by curves 2–5, characterised by continuous variation of the oxygen absorption rate.

The presence of a long period in which the kinetic law $\exp(\Phi t)$ is fulfilled does not exhaust the specific features of the oxidation of polymers with enhanced thermofluctuation mobility of the molecular sponge. Yet another feature is the substantial dependence of the reaction rate on the pressure of oxygen in the 26–100 kPa range⁷⁵ (the rate of oxidation of liquid hydrocarbons in this range is close to the limiting value).

In addition, it can be seen from Fig. 6 (curves 2, 4) that this oxidation mode is characterised by a high limiting concentration of POOH, which barely changes for a long period of time. Unlike this situation, in the oxidation of high-molecular-mass polyolefins (and quite often, of low-molecular-mass liquid hydrocarbons), the

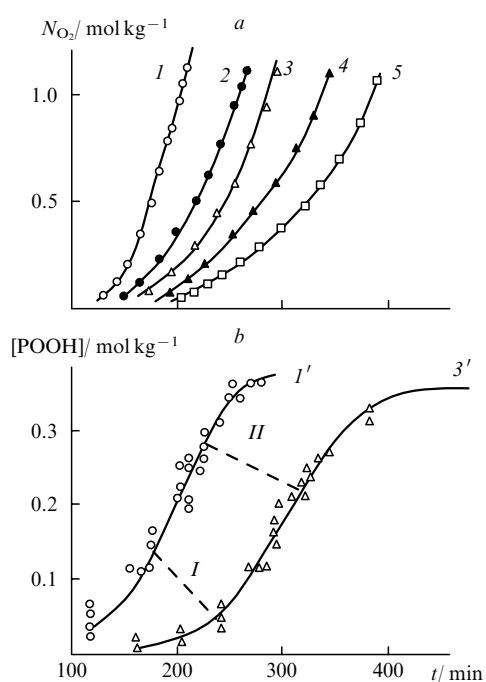


Figure 17. Variation of the amount of oxygen absorbed (*a*) and hydroperoxide accumulated (*b*) in the initial (non-oriented) polymethylpentene film (1, 1') and in films stretched to a ratio of 4 (2), 6 (3, 3'), 9 (4) and 12 (5) during oxidation at 130 °C and an oxygen pressure of 80 kPa.⁷⁶

POOH concentration passes through a relatively sharp maximum, which appears due to the decomposition of hydroperoxide induced by organic acids, which accelerates with time. The carboxylic acids formed in large amounts in the oxidation of liquid cyclohexane, *n*-decane⁷⁷ and nonene⁷⁸ destroy another oxidation product, hydroperoxide, its maximum concentration being thus limited to ~0.3, 0.2 and 0.4–0.5 mol kg⁻¹, respectively.

However, oxidation of a melt of low-molecular-mass APP and orientationally drawn IPP films gives POOH and polymeric ketones as the major products, whereas the yield of acids is insignificant.²⁶ It is the low concentration of acids that accounts, in all probability, for the absence of sharp maxima in curves 2, 4 in Fig. 6. The presence of a concentration limit in these curves can be regarded as evidence for the occurrence of chain decomposition of POOH under the action of free radicals. The rate of chain decomposition of POOH corresponding to this limiting concentration should be equal to the rate of its chain formation, the quasi-steady-state concentration of radicals that induce the decomposition remaining virtually constant for a long period.

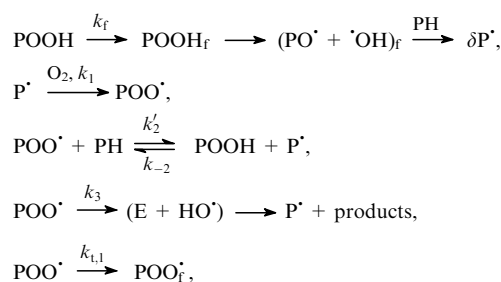
Yet another important feature of the oxidation of low-molecular-mass APP is the fact that the kinetic laws of the cleavage of the macromolecules established by Iring *et al.*²⁶ using the gel-chromatographic method for the determination of the molecular mass distribution do not coincide with the kinetic laws established by Ivanov *et al.*,⁷⁵ who used a variant of osmometry.

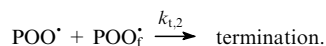
For example, in the former study,²⁶ in which the oxidation of APP was carried out at a high pressure of oxygen (10³ kPa), the number of breaks in the polymer chains increased according to the same law as the amount of absorbed oxygen and was equal to 0.01 mol litre⁻¹ at 120 °C over a period of 50 min, while in the latter study,⁷⁵ in which APP was oxidised at $P_{O_2} \leq 100$ kPa, the number of breaks was 0.033 mol litre⁻¹ over the same period of time. The rate of polymer chain scission remained constant during the whole process (Fig. 16 *b*), although it was directly proportional to the pressure of oxygen. In this particular case (when the pressure of oxygen is low) more intense degradation takes place due to the cleavage of those macroradicals the concentrations of which do not depend on the oxidation time or on the concentration of POOH formed.

The factors listed above give grounds for claiming that neither the model of homogeneous oxidation of hydrocarbons nor the models of heterophase oxidation of high-molecular-mass polymers, considered in the preceding Sections, are suitable for describing the oxidation of molten low-molecular-mass APP. The law $\exp(\Phi t)$ characterising the self-accelerated stage coincides only formally with the regularity established for gas-phase reactions with avalanche-like branching of reaction chains. In the condensed phase, the avalanche-like chain branching is impossible for several reasons reported in the literature.⁷⁹

Thus, a kinetic model for the oxidation of polymers distinguished by high thermofluctuation mobility of the molecular sponge should take into account the structural and physical changes of the chemical quasi-elementary steps, specific for the given state, which are actually heterogeneous.

The high frequency of excitation of f-nanopores in a spongy matrix makes it possible to propose the following scheme of the frequency-modulated oxidation process





By applying the condition of steady-state concentrations of free radicals, one can easily find the concentration of peroxy radicals $\text{POO}^\bullet$, involved in the oxidation chains, which will be referred to as linear chains

$$[\text{POO}^\bullet] = \frac{\delta k_f [\text{POOH}]}{2k_{t,1}}$$

(δ is the yield of macroradicals in the decomposition of POOH_t), the concentration of alkyl macroradicals

$$[\text{P}^\bullet] = \frac{0.5\delta k_f [\text{POOH}](k_2 + k_3)}{k_{t,1}(k_1[\text{O}_2] + k_{-2}[\text{POOH}])},$$

the rate of accumulation of POOH , which is made up of the rates of chain formation, chain decomposition and spontaneous decomposition

$$\begin{aligned} \frac{d[\text{POOH}]}{dt} &= \frac{0.5\delta k_f [\text{POOH}]}{k_{t,1}} - \frac{0.5k_{-2}(k_2 + k_3)\delta k_f [\text{POOH}]^2}{k_{t,1}(k_1[\text{O}_2] + k_{-2}[\text{POOH}])} \\ &\quad - k_f [\text{POOH}] = \Phi [\text{POOH}] - \frac{\Phi [\text{POOH}]^2}{\varphi(\chi + [\text{POOH}])}, \end{aligned} \quad (26)$$

and the rate of oxygen absorption (the contribution of the spontaneous decomposition of POOH can be neglected)

$$-\frac{d[\text{O}_2]}{dt} = \frac{d\Delta[\text{O}_2]}{dt} = k_1[\text{P}^\bullet][\text{O}_2] = \frac{\Phi \chi [\text{POOH}]}{\varphi(\chi + [\text{POOH}])}, \quad (27)$$

where $\Phi = k_f(0.5\delta k_f k_{t,1}^{-1} - 1) \approx 0.5k_2\delta k_f k_{t,1}^{-1}$, $\varphi = k_2(k_2 + k_3)^{-1}$, $\chi = k_1[\text{O}_2]k_{-2}^{-1}$.

It follows from Eqn (26) that at the beginning of the self-accelerated oxidation stage, when $d[\text{POOH}]/dt = \Phi[\text{POOH}]$, the content of POOH increases with time by an exponential law

$$[\text{POOH}] = [\text{POOH}]_t \exp(\Phi t),$$

where $[\text{POOH}]_t$ is the concentration of POOH at the end of the induction period.

During this period, the rate of oxygen absorption also increases according to an exponential law in view of the relation $[\text{POOH}] < \chi$:

$$\frac{d\Delta[\text{O}_2]}{dt} = \frac{\Phi [\text{POOH}]}{\varphi} = \frac{\Phi [\text{POOH}]_0}{\varphi} \exp(\Phi t). \quad (28)$$

The Φ , φ , and χ values were found by solving the set of differential equations (26) and (27) using the simple Euler method.⁵² The results of calculations were compared with experimental data presented in Figs 6, 16 and 17.

The theoretical curves 1 and 2 in Fig. 6, corresponding to low-molecular-mass APP, are in agreement with experimental data obtained by Iring *et al.*²⁶ The Φ , φ , χ and $[\text{POOH}]_t$ values corresponding to these curves are

$$\Phi = 0.034 \text{ min}^{-1}, \varphi = 0.5, \chi = 1.1 \text{ mol litre}^{-1}, \\ [\text{POOH}]_t = 0.02 \text{ mol litre}^{-1}.$$

The theoretical curves 3 and 4 in Fig. 6, which refer to IPP films stretched orientationally by a factor of 5, are also in good agreement with experimental points. The corresponding coefficients are

$$\Phi = 0.027 \text{ min}^{-1}, \varphi = 0.4, \chi = 1.05 \text{ mol litre}^{-1}, \\ [\text{POOH}]_t = 0.02 \text{ mol litre}^{-1}.$$

The qualitative difference between curves 3, 4 and curves 1, 2 is associated with the appearance of an induction period with $\tau = 200$ min in the oxidation of oriented films (in the case of a melt, $\tau \approx 0$ min).

Figure 16 shows the theoretical curves corresponding to the oxidation of an APP melt at a lower pressure $P_{\text{O}_2} = 100$ kPa. They are also in good agreement with experimental data⁷⁵ with the following coefficients Φ , φ and χ :

$T/^\circ\text{C}$	Φ/s^{-1}	φ	$\chi/\text{mol litre}^{-1}$
120	1.0×10^{-3}	0.5	0.4
130	1.8×10^{-3}	0.5	0.4
140	3.6×10^{-3}	0.5	0.4

The calculations were performed with the assumption that the yield of POOH per mole of oxygen absorbed in linear chains does not depend on temperature and corresponds to the φ value taken from a study by Iring *et al.*,²⁶ the $[\text{POOH}]_t$ value remains equal to $0.02 \text{ mol litre}^{-1}$, and the limiting concentration of the hydroperoxide, needed to estimate the coefficient χ , is $[\text{POOH}]_{\text{lim}} = 0.4 \text{ mol litre}^{-1}$.

Taking into account the variation of the coefficient Φ vs. temperature and using the Arrhenius equation, one can calculate the effective activation energy $E_\Phi = 86.0 \text{ kJ mol}^{-1}$. This value differs from the effective activation energy of scission found from Fig. 16 b ($E_n = 106.0 \text{ kJ mol}^{-1}$).

The thermomechanical modulation of the chemical events is also manifested in the experiments with oriented polymethylpentene films (Fig. 17). As in the case of oriented IPP films, the modulation is due to the enhancement of the molecular-segment mobility as a result of relaxation of internal stress. The qualitative difference between curves 1, 1', describing the oxidation of isotropic films, and curves 3, 3', which refer to oriented films can be clearly seen in Fig. 17. Curves 3 (Fig. 17 a, oxygen absorption) and 3' (Fig. 17 b, POOH accumulation) were constructed by solving the set of equations (26) and (27). For $\Phi = 0.03 \text{ min}^{-1}$, $\varphi = 0.13$, $\chi = 2.4 \text{ mol kg}^{-1}$, $[\text{POOH}]_t = 0.01 \text{ mol kg}^{-1}$ and $\tau = 160$ min, they are in good agreement with experimental data reported by Rapoport *et al.*⁷⁶ (130°C , $P_{\text{O}_2} = 80$ kPa).

It should be noted that the yield of hydroperoxide φ in oriented films permanently varies during oxidation. Indeed, it can be seen in Fig. 17 b, which shows the curves for 0.5 (curve I) and 1.4 mol kg^{-1} (curve II) of absorbed oxygen, that $\varphi = 0.1$ at the point of intersection of curves I and 3' and $\varphi = 0.16$ at the point of intersection of curves II and 3'. The value $\varphi = 0.13$ assumed in our calculations is the average of these two values.

The fact that the parameter φ (and, hence, χ) depends on the draw ratio and on the degree of oxidation suggests that the good agreement between the calculated and experimental data for oriented films results, most likely, from a favourable superposition of the chemical reaction and structural relaxation. In other cases, this agreement may be missing and the process kinetics would undergo substantial changes.¹⁴ Nevertheless, the results indicate that the principle of structure-mechanical modulation of chemical steps is correct at the qualitative level.

The scheme of chemical transformations analysed in this Section differs from the heterophase schemes considered previously not only by the fact that it includes the steps of free radical generation in enlarged f-nanopores but also by the fact that it assumes decomposition of POOH induced by alkyl macroradicals (characterised by the constant k_{-2}) and quasi-linear termination of oxidation chains in f-nanopores [Eqn (18)].

The induced decomposition of POOH can also account for both the presence of the concentration limit in the accumulation of the hydroperoxide and the influence of the pressure of oxygen on the oxidation rate. The latter is due to the competition between oxygen and hydroperoxide for the alkyl macroradicals, which are converted in linear oxidation chains (see above).

According to published data, in liquid-phase systems under conditions of oxygen deficiency, the contribution of the reaction of alkyl radicals with hydroperoxide to the overall scheme is fairly high. This has been explained by the 'abnormally' high rate of the abstraction of hydrogen atoms from hydroperoxide groups by the attacking alkyl radicals.^{70, 71} Previously, based on the idea of

competition between the process acceleration due to the increase in the oxygen concentration and the process retardation due to the increase in the mechanical pressure of the gas phase.

Thus, the mechanical pressure of the gas atmosphere on the chain-segment sponge of the polymers being oxidised should be taken into account as necessarily as is the structural and mechanical previous history of samples and the internal stress relaxation.

IX. Cross-linking of polyolefin macromolecules

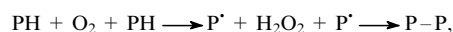
Oxidation of polyolefins is accompanied not only by chain scission according to one of the mechanisms considered above but also by the formation of chain cross-links. Cross-linking increases the molecular mass of the polymer and the number of points of branching on individual chains and creates a three-dimensional network, which, under certain conditions, can produce a gel fraction insoluble in liquids. Experimental data available from the literature make it possible to consider the oxidative cross-linking of polyolefins in terms of the micellar-sponge model of the polymeric matrix.

The redistribution of the molecular masses of molecules in an LDPE melt and solid-like IPP films during their oxidation at 130–160 °C has been studied.^{5,82,83} Analysis of the molecular-mass distribution (MMD) by gel permeation chromatography showed that even absorption of a slight amount of oxygen changes the molecular masses of IPP and LDPE, the patterns of these changes being different for these two polymers.

During the oxidation of molten LDPE, rupture of macromolecules predominates in the induction period over a broad range of oxygen pressures; a slightly pronounced tendency for the enlargement of macromolecules is detected only for very low pressures ($P_{O_2} \leq 2.6$ kPa).⁸²

However, in the case of IPP at $P_{O_2} = 10.6, 80.0$ and 101.3 kPa, scission and cross-linking of molecules proceed in the induction period at comparable rates. This gives a bimodal MMD (having two peaks, one at higher and one at lower molecular masses); the yield of the higher-molecular-mass fraction increases as the pressure of oxygen diminishes. As oxidation advances, the high-molecular-mass fraction of IPP becomes involved in the degradation process and an unimodal distribution is established, the MMD maximum being shifted towards lower molecular masses.^{5,82,83} In this case, the enlargement of molecules is transient.

No clear view on the mechanism of transient cross-linking can be found in the literature. It has been suggested^{5,83} that it is due to the termolecular reaction



yielding two macroradicals, which recombine in a 'cage'. In the opinion of the researchers cited,^{5,83} this assumption is supported by the fact that the yield of cross-linked macromolecules increases upon orientational drawing, which prevents radicals from leaving the cage.

For instance, when isotropic and oriented IPP samples absorb equal amounts of oxygen (0.14 mol kg⁻¹, 130 °C, $P_{O_2} = 78$ kPa), the average molecular mass of isotropic IPP decreases from 3.0×10^5 to 0.6×10^5 , while the molecular mass of IPP films stretched 10-fold, conversely, increases from 3.0×10^5 to 6.3×10^5 . However, during further oxidation of the stretched films degradation becomes the predominant process. It will be shown below that the transient cross-linking of IPP molecules occurs in s-zones and involves the alkyl macroradicals and the C=C bonds formed in these zones. This is facilitated by the deficiency of free oxygen molecules, typical of s-zones.

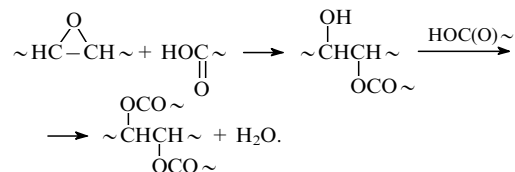
The transient cross-linking of molten polyethylene in the beginning of oxidation barely influences the molecular mass of the polymer; however, the formation of the macromolecular network is manifested in full measure in the macroscopic kinetic stage that comes after fairly extensive destruction.^{84,85} The process of destruction preceding the formation of the molecular

network involves a 200- to 600-μm thick layer of the melt, depending on the temperature (230–150 °C, respectively). This results in a substantial (5–15-fold) decrease in the molecular mass of the polymer; as a consequence, the oxidised polymer becomes waxy.⁸⁵ The cross-linking of molecules during further oxidation of the destroyed material proceeds in an autocatalytic mode and yields a 30–160-μm cross-linked shell.

It has been emphasised⁸⁵ that cross-linking of the oxidised material starts simultaneously throughout the whole relatively thick near-surface layer (80 μm at 150 °C), although the sources of free radicals, POOH groups, are distributed in this layer non-uniformly, their concentration decreasing on moving away from the surface. The amount of the gel fraction in the oxidised polyethylene increases over some period of time. During this period, a densely cross-linked crust is formed. The process continues until almost all macromolecules are incorporated in the molecular network structure. The density of the gel fraction at the end of the process reaches 1 g cm⁻¹.

No clear views on the mechanism of this process can be found in the literature. A rather obvious reaction is condensation of carboxylic acids with secondary alcohols.⁸⁶ However, the mechanisms of formation of the acids and the alcohols are not discussed.

Meanwhile, the fact that cross-linking starts only after accumulation of a particular amount of the oxidised fragments of polyethylene molecules suggests that this process can be associated with the condensation of carboxylic acids with epoxides, formed as intermediate oxidation products (see Section IV), the concentration of which does not depend on the content of POOH:



In accordance with the heterophase structure of the polymeric molecular-sponge microreactors (see Fig. 7), the condensation cross-linking should occur in the v-zones of the micelles, which accumulate the main bulk of oxygen-containing oxidation products, as opposed to the transient cross-linking, which occurs in s-zones.

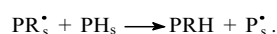
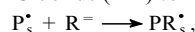
The condensation, considered in terms of the heterophase model, becomes possible only at a substantial degree of oxidative degradation (after a required amount of acid residues has been accumulated). The condensation can account for the self-accelerated character of cross-linking, which is due to the permanent increase in the acid concentration and for the fact that this process virtually does not depend on the distribution of POOH over the layer depth. This is confirmed by the appearance of ester groups at high degrees of oxidation of molten polyethylene and by their subsequent self-accelerated accumulation (which was demonstrated by NMR⁴⁹ and IR spectroscopy⁸⁴). The complete solubility of the gel fraction in strong alkalis and acids proves that the cross-links in the molecular network are actually formed by ester groups.⁸⁴

Let us consider once again the transient cross-linking, which manifests itself most clearly for IPP films stretched 10-fold. It should be noted that the number of cross-links observed in practice under conditions most favourable for the termolecular reaction is 1000 times greater than the value calculated theoretically.⁸ Therefore, Denisov⁸ proposed that the addition of alkyl and peroxy macroradicals to the C=C bonds, always present in polyolefins in small amounts, should also be included in the consideration.

However, this assumption does not agree with the kinetics of cross-linking of polymer chains in oriented IPP films. Indeed, in the oxidation of 10-fold stretched films, the cross-linking starts only 75 min after the reaction has begun but before the induction period has been over ($\tau = 100$ min at 130 °C and $P_{O_2} = 78$ kPa). During these 75 min, the mean mass of molecules remains

constant.^{5, 83} Thus, cross-linking involves only unsaturated C=C bonds, which accumulate during oxidation.

The transient cross-linking of the IPP molecules might occur by a chain mechanism,⁸⁷ which has been established previously for the cross-linking of polyethylene molecules initiated by dibenzoyl peroxide. According to this mechanism, cross-links are formed due to the addition of macromolecule fragments having terminal C=C bonds ($R^{\cdot}$) to internal macroradicals ($P_s^{\cdot}$):



By adding these reactions to the overall scheme of the process occurring in the s-zones of the matrix in the induction period (see Section IV.1) and by using the steady-state concentration conditions for free radicals, one can easily see that these reactions do not change the form of the equation describing the concentration of the $R_s^{\cdot}$ radicals, responsible for the s,v-translation of free valence

$$[R_s^{\cdot}] = \frac{\delta k'_{0s}[PH_s][O_{2s}]}{2k_{1s}}.$$

The rate of initiation of the oxidation chains in the v-zones of matrix micelles does not change either.

The validity of the above scheme for the transient chain cross-linking of the IPP molecules is supported by the fact that the rate of this process increases upon orientational drawing of films. Drawing is known to be accompanied by fibrillation of polymer chains, which are reorganised to give bundles (about tens of angstroms in diameter) and acquire enhanced highly elastic tension.^{5, 88} Despite dense packing, the fibrillar units are separated from one another by clear-cut interfaces, which can be clearly seen in the micrographs taken by an electron microscope.

Judging by the structure of spongy micelles (Fig. 7), one can expect that uniaxial drawing of a polymer film would result in the transformation of spherical grains into ellipsoids filled with fibrils of stretched chains. The mobility of chain units inside the fibrils would decrease and the nanopores in them would become even narrower. However, the interfaces between the fibrils would actually represent newly formed zones of s-nanopores. The increase in the number and the volume of zones filled with s-nanopores should naturally increase the contribution of reactions which occur in these zones including chain cross-linking.

It has been noted that cross-linking lags somewhat behind the rupture of IPP macromolecules. This is due to the fact that the structure-mechanical stabilisation of fibrils in the supermolecular framework depresses for some period the mobility of the fragments of macromolecules with terminal C=C bonds. A definite number of polymer chain scissions is required in order to weaken the rigid mechanical fixing of fragments in the framework structure. During this period, some C=C bonds are accumulated in the interfibrillar layers, and, as the chemically induced relaxation of internal stress goes on, rapid formation of the cross-linked network starts by the radical chain mechanism described above

X. Oxidation of fibrillised polyolefins

The change in the structure of the spongy micellar matrix induced by fibrillation influences the dynamic characteristics of a paramagnetic probe — stable free radical, 2,2,6,6-tetramethylpiperidin-1-oxyl — introduced in a polymer. The behaviour of the nitroxide depends on when it is introduced into the sample.^{5, 89} If the radical probe is introduced initially and then the sample is drawn, the probe is fixed in a low-mobility state with appreciably hindered rotational and translational motion. However, if the radical probe is introduced into the films after drawing, it populates the accessible areas of the matrix and displays high frequency of rotation and high rate of migration through the matrix.

Owing to the spongy micellar structure of the matrix, the radical probe added before the film drawing is absorbed during

drawing in fairly narrow nanopores of the fibrils being formed and is not displaced into the interfibrillar layers. Conversely, the radical probe added after fibrillation is unable to penetrate inside the fibrils and mainly occupies s-nanopores in the interfibrillar layers.

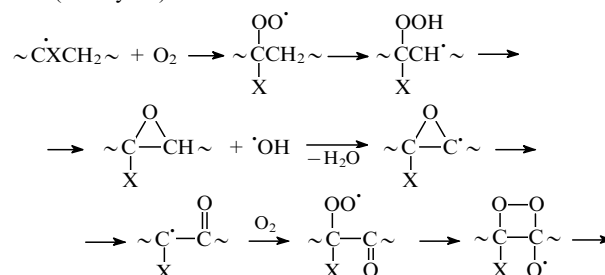
It is obvious that the structural rearrangement induced by drawing should necessarily change the kinetics of oxidation. Indeed, the fairly strong fixing of fibrils due to restructurisation of the crystallite framework can substantially extend the induction period of oxidation by decreasing the frequency of the steps of s,v-transfer of free valence and migration of hydroperoxide groups from the inner space of fibrils to interfibrillar s-nanopores. This situation is observed in the oxidation of highly crystalline IPP, HDPE and polymethylpentene.^{5, 35, 76}

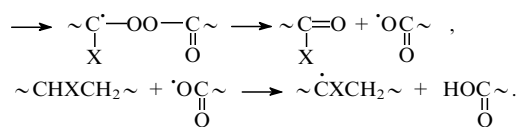
It is typical that the induction period disappears if IPP films have been subjected to non-extensive oxidation (up to the accumulation of $\sim 0.02 \text{ mol kg}^{-1}$ of POOH) prior to drawing.⁵ This fact contradicts the assumption, made in the same study,⁵ that drawing enhances the cage effect (*i.e.* decreases the yield of radicals in the dissociation of POOH) but it is in line with the 'bottle-neck' effect in both the forward and backward phase transfer chemical induction processes.

In fact, orientational drawing of non-oxidised films increases the induction period for the structural and mechanical reasons indicated above, whereas drawing of pre-oxidised films, without changing the content of POOH in the previously oxidised s-zones, increases the number of new interfibrillar s-zones, to which hydroperoxide is displaced from the inner bulk of fibrils during their formation. With this type of sample processing, oxidation is effected from the very beginning by vigorous scission of macromolecules and by chemically induced relaxation of internal stresses; this accounts for the absence of a noticeable induction period.

Study of IPP and HDPE films by local IR spectroscopy (by scanning samples by a beam with a 1-mm^2 cross-section) showed that oxidation of oriented films with mechanically fixed ends occurs non-uniformly over the area of the sample and has different rates in different local zones. The ratio of the carbonyl products of oxidation changes.⁵ Note that in conventional IR spectra of oxidised fibrillised samples, the intensities of the absorption bands at about $1740\text{--}1745$ and $1770\text{--}1780 \text{ cm}^{-1}$, which correspond to ester and lactone groups,^{86, 90} are greater³⁵ than the intensities of the absorption bands at $1710\text{--}1720 \text{ cm}^{-1}$, due to acids and ketones.

Qualitatively, the process can be represented as follows. The primary reaction chains are originated in the interfibrillar s-zones. They include the steps of scission and cross-linking of s-units, which ensure restructurisation of interfibrillar layers and thus increase the elastic load on the fibrils. These processes result in the appearance of free valences, translated with a low frequency to the narrow internal nanopores of the fibrils. Due to the narrowness of the pores and the high-elasticity tension of the polymer molecules in the fibrils, the peroxy radicals formed under these conditions undergo mainly β -isomerisation to give epoxide rings and free hydroxyls. The hydroxyl and the epoxide, which are unable to separate widely in a narrow nanopore, react with each other; this gives rise to the non-hydroperoxide oxidation pathway leading to ketones (aldehydes) and acids





Rupture of an individual polymer molecule in the structure of an elastically stretched fibril affords fragments which relax independently to the most equilibrium conformation by transferring the mechanical load to the surrounding molecules and enhancing their tension. Thus, narrow nanopores having an increased length appear inside the fibrils; they serve simultaneously as the sites of accumulation of the oxygen molecules expelled from the neighbouring layers of the intrafibril sponge.

The subsequent reactions inside the newly arisen relaxation site of oxidation include the transfer of free valence over its surface in accordance with the above scheme. Under these conditions, carboxy and epoxy groups are formed in the vicinity of each other; they react to give ester groups. Thus, orientational drawing of IPP and HDPE creates conditions for the formation of esters in the relaxation intrafibril sites even at early oxidation stages, whereas in the case of isotropic polyethylene melts, esters are formed only after fairly extensive oxidative destruction has taken place (see Section IX).

An important feature of oxidation in the relaxation sites inside the fibrils is that the removal of fragments of macromolecules from these sites facilitates the arrival of free radicals at the intact polymer chains, which remain in the stretched state. As a consequence, the process propagates predominantly across the fibril, and the intermediate polymeric peroxy radicals participating in the process are rigidly fixed at the elastically stretched macromolecules; thus, they are mainly converted without the formation of POOH.

The continuous accumulation of structural damages inside the fibril and enhancement of the load on the remaining oriented chains should result sooner or later in the rupture of the fibril and in the abrupt relief of the elastic strain. The sharp increase in the beating mobility of a nanopore in the fibril fragments substantially increases the probability of intermolecular propagation of oxidation chains accompanied by the formation and simultaneous dissociation of POOH. In other words, upon the relief of mechanical stress, oxidation sharply accelerates becoming a local chemical outburst and efficiently influences the surrounding matrix both by transferring mechanical load and injecting chemically reactive species therein.

During further oxidation, fragmentation involves initially the separate macroscopic areas and then the whole oriented sample, whose ends are mechanically fixed. As a consequence, a backbone crack grows through the sample cross-section, which fractures the sample, and oxidation passes to the self-accelerated stage.⁵

The kinetic, structural and mechanical features of oxidation listed above have been observed in experiments with polyolefin films subjected to uniaxial orientational drawing. Commercial polymeric articles produced by extrusion, moulding and hose blowing have micellar structures. The structural lability of molecular spongy micelles and the ability of the crystalline framework to be reorganised account for the appearance of uncontrolled internal stresses and local deformations accompanied by fibrillation, taking place in these articles to one or another extent.

The structural and mechanical inhomogeneities introduced into the articles at the stage of processing of polymer ingredients are the reason for the change of the physical properties of articles during performance and storage.⁹¹ Even minor external mechanical action (during cooling of the melt) induces the layer structural inhomogeneity of the material, caused by the relaxation mechanism of heat removal and non-uniform temperature distribution over the material thickness.⁹²

This should lead to non-reproducibility of the quantitative results of kinetic studies, which is typical of these materials. This is illustrated by numerous experimental data (see Ref. 93 and references therein), which show that the durations of the induction

periods and the amounts of accumulated products in the oxidation of IPP and LDPE vary over wide limits, depending on the previous history and thickness of samples manufactured by industrial technologies.

The diversity of factors which influence in one or another way the internal structure of polymeric articles makes very difficult the task of constructing a unified kinetic model of oxidation, which would provide a quantitative description for both laboratory specimens and commercial materials. However, we hope that the oxidation models proposed here would lay a more reliable foundation for the analysis of particular processes of ageing and stabilisation of polymers than liquid-phase models, which are not quite applicable to polymers.

XI. Conclusion

The purpose of this review is to demonstrate the principles of structure-kinetic modelling of chain oxidation reactions occurring in a non-crystalline polymeric matrix. A molecular spongy micelle, an important element in the framework structure of a noncrystalline polymer, was chosen as the morphological basis for modelling.

The kinetic model developed with allowance for the nanoscale micellar heterophase structure has already explained a series of specific features of free radical chain transformations which cannot be explained in terms of homogeneous reaction models.^{15, 16, 18–22, 38, 94} This model was used to interpret the mechanisms of separate stages of the oxidation of polymers described by kinetic laws different in kind. These stages either replace one another during the process or are changed themselves due to the change in the thermomechanical state of the polymeric object.

The structure-mechanical reasons for the curious features of initiated oxidation, which do not fit in the homogeneous reaction models, were identified. The morphological and structure-kinetic models used here impart definite meaning to the concept of structure-mechanical modification of the chemical reactivity of species reacting in a molecular spongy matrix, which is considered as a process directly related to the molecular-segment lability and flickering mobility of nanopores.

It should be emphasised that the heterophase models considered here not only disclose the physical essence of each oxidation stage but also identify the relationship between the chemistry of transformations and the most important structural properties of the molecular spongy matrix, thus extending the morphological basis of the chemical physics of polymers.

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Relaxation properties of polymers and the physical network model

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Abstract. The role of the physical network in the dynamics of macromolecules is considered. It is shown that experimental data are often inconsistent not only quantitatively but also qualitatively with the results obtained in terms of the widespread reptation model based on the concept of network entanglement. Evidence is given indicating that the network of physical bonds is the governing factor in the dynamics of macromolecules. The bibliography includes 218 references.

I. Introduction

The condensed state of substances is determined by the nature of intermolecular interactions. This statement appears trivial; however, in the case of polymers the situation is not that simple. Indeed, below the glass transition temperature, the properties of a high-molecular body virtually do not differ from those of a low-molecular body (the latter may be brittle), whereas in the high-temperature range they differ rather substantially. This is primarily due to the chain nature of the molecules owing to which polymers display properties which allow one to speak about their specific (highly elastic) state; network structures are only possible in polymeric bodies; it is in the polymers that such a structural level as the topological one is the most important. Thus, intermolecular interactions in high-molecular-mass compounds cannot be reduced only to the formation of more or less strong bonds of an energetic nature. In order to understand and describe properties of polymeric substances, it is necessary to take into consideration topological features of their structures.

The use of the concept of physical networks¹ allows a more adequate description of polymers: energetic interactions are assumed to be localised at certain points regarded as nodes, whereas the topological aspects of the structure are interpreted

with the aid of terminology used to describe covalent networks (*e.g.*, internodal chains, tails, gel and sol fractions, *etc.*).^{2,3} Any polymeric system can be described as a network whose nodes have a finite lifetime. The concentration of nodes depends on external conditions: temperature, strain, the presence of a solvent.

Physical networks, usually called gels, are fairly well studied subjects.^{4–7} According to Flory,⁸ they can be classified as follows: well-ordered lamellar structures, including gel-like mesophases; totally disordered polymeric networks; polymeric networks formed by physical aggregation which are mostly disordered but comprise some ordered regions; and specific disordered structures.

This classification comprises covalent network polymers but does not include non-crosslinked polymers. This is due to the fact that in the cases under consideration the nodes of physical networks are represented by certain microphase structures. Common linear or branched polymers devoid of such structures, though not being called gels, exhibit, in definite temperature and time intervals, properties of gels, which are in particular exhibited in the relaxation of the elasticity modulus. Consequently, when considering all polymers, one can make recourse to the above-mentioned Flory classification complemented with disordered polymeric systems comprising the nodes whose nature differs from that of microphases.

At present, the most popular viewpoint is that the nodes of a physical network are entanglements, *i.e.*, units of topological and entropic rather than energetic origin.^{9–13} However, it should be noted that in this case too, the concentration of nodes depends on temperature, although the heat of node formation is rather small, $\sim 9 \text{ kJ mol}^{-1}$.¹⁴

The polymers containing functional groups capable of forming sufficiently strong energetic bonds (of the hydrogen bond type) can be regarded as an intermediate case, if these groups are distributed along the chain in a manner, which prevents the formation of ‘zones of physical bonds’.¹⁵ According to the Flory classification, the first group of physical networks is macromolecular in essence. Therefore, if the network polymers are excluded, then all the polymeric systems regarded as physical networks may be classified as follows:

(1) networks with nodes of a microphase type which have ordered or disordered structures;

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(2) networks with nodes formed by strong intermolecular bonding of the hydrogen bond type;

(3) networks with nodes of entropic (topological) nature.

The first group comprises systems which are commonly regarded as physical gels. Numerous papers and reviews have been devoted to the thermodynamic aspects of such systems and their phase structure.^{4–8, 15} The role of energetic intermolecular interactions in these systems has been established.

All other polymers may be included into the second and mostly the third groups. An important point here consists in estimating the contribution of the energetic component and intermolecular interactions to the properties of polymeric systems of these types.

II. The role of topological factors. The reptation model

A distinctive feature of polymeric systems consists in the existence of the highly elastic state which is manifested in that they exhibit properties of an elastic body over definite time and temperature intervals: above the glass transition temperature and below the flow temperature, one observes a high-elasticity plateau in the relaxation curves. In this range, the real part of the elasticity modulus is slightly dependent on the temperature and time (frequency of measurements) of the experiment; consequently, the plateau is of the entropic rather than energetic origin. It is noteworthy that the above-mentioned weak dependence is relative, because in the interval of low temperatures and high frequencies (short times) the high-elasticity plateau is superimposed on the glass transition region. For this reason, it is sometimes difficult to establish whether the changes in the elasticity modulus are associated with this circumstance, or this parameter depends *per se* on the temperature and time of the experiment in the plateau region.

Evidence in favour of the entropic nature of intermolecular interactions which determine properties of the polymeric systems is provided by the dependences of the range of the high-elasticity plateau and the viscosity of melts and concentrated solutions of polymers on their molecular masses (MM).

The theories which substantiate the above dependences (see, e.g., Refs 10, 13, 16–18) are based on the concepts of crucial role of the network of physical (topological) nodes, while the network connectivity (critical conditions of the network appearance) depends on the length of the chains that are cross-linked the correlation between theoretical predictions of basic regularities of diffusion and relaxation in such systems and experimental results requires that some refinements of the type of ‘constrain release’ and ‘tube relaxation or tube renewal’ are introduced.^{19, 20}

The simplest version¹³ of the reptation model describes the dynamic properties of a polymer melt in terms of the Rouse theory (R) if MM is smaller than a certain critical value M_c . In this case, the viscosity η should be proportional and the diffusion coefficient D inversely proportional to MM; hence, the product ηD is independent of MM. The dynamics of a macromolecule is determined by two characteristic scaling parameters: the segment length l and the mean square radius of the macromolecule coil $\langle R^2 \rangle^{1/2}$. The dependence of the squared displacement of the central segment of the chain on time $g_m(t)$ obeys the following relations:

$$g_m(t) \propto \begin{cases} t & \text{if } g_m < l^2, \\ t^{1/2} & \text{if } l^2 < g_m < \langle R^2 \rangle, \\ t & \text{if } g_m > \langle R^2 \rangle. \end{cases} \quad (1)$$

At $MM > M_c$, the crucial role is played by the third scaling parameter, i.e., the mean square radius of the chain between entanglements or the ‘tube’ radius $\langle R_e^2 \rangle^{1/2}$. The dependence of viscosity and maximum relaxation time on MM should be exponential with the exponent equal to 3. The diffusion coefficient decreases proportionally to the squared MM; consequently, the product ηD is proportional to MM. The squared displacement of

the central segment of the chain as a function of time $g_m(t)$ is determined by the following relations:

$$g_m(t) \propto \begin{cases} t & \text{if } g_m < l^2, \\ t^{1/2} & \text{if } l^2 < g_m < \langle R_e^2 \rangle, \\ t^{1/4} & \text{if } \langle R_e^2 \rangle < g_m < \langle R^2 \rangle, \\ t^{1/2} & \text{if } \langle R^2 \rangle \frac{N}{N_e} > g_m > \langle R^2 \rangle, \\ t & \text{if } g_m > \langle R^2 \rangle \frac{N}{N_e}. \end{cases} \quad (2)$$

where N is the chain length and N_e is the chain length between entanglements.

Predictions of the dynamics of macromolecules have been the subject of both numerous experimental studies^{10, 14–23} and computer simulations.^{24–38} In the latter case, the energy factor was not, as a rule, taken into account, since it was believed that only the excluded volume (the ‘repulsive’ part of the interaction potential) and impermeability of chains are significant. Unfortunately, there are virtually no studies (except for the investigations^{29–32} on the behaviour of low-molecular chains of the type of paraffin oligomeric chains) in which the ‘attractive’ part of the interaction potential has been estimated. In short, ‘...the reptation hypothesis and models built thereon give an extremely good qualitative description of a broad range of experimental observations; in many cases, the agreement is quantitative. ...If it is more important for a good model to explain a wide variety of phenomena reasonably well than to be in precise agreement with a restricted set of observations, then reptation-based models must be viewed as extremely successful’.¹⁹

The existence of topological nodes in the structure of polymers is proved by their fixation upon cross-linking of linear polymers.³³ At a sufficiently high degree of cross-linking, the total number of nodes as determined from physical measurements exceeds the number of nodes calculated from the conditions of a chemical experiment by an amount which presumably corresponds to the number of entanglements (topological nodes) in a non-cross-linked system.²

For a number of polymeric systems^{2, 39, 40} this finding was confirmed experimentally and by computer simulation.^{41–44} However, there are data (see, e.g., Ref. 45) which disprove this view.

Thus, it would seem that there are no reasons for casting doubts on the existence of entanglements as structural units and their role in the formation of relaxation properties of polymers. However, a detailed analysis of experimental results shows that such reasons exist.

III. Correlation between viscosity and viscoelasticity

It is usually assumed that the character of the dependence of viscosity on MM, a kink in the curve in the vicinity of certain ‘critical’ value of M_c ⁴⁶ and the appearance of a high-elasticity plateau[†] are determined by the same factor, viz., by the presence of topological nodes or entanglements of polymeric chains.¹⁴ Therefore, it is natural to suggest if not equality, at least a correlation between the parameters M_e and M_c . However, back in 1974, Graessley¹⁷ noticed that such a correlation does not exist and, what is more, the M_e values found from the results of viscosity and compliance measurements are conflicting. Having analysed 70 polymers, Aharoni⁴⁹ showed that despite the absence of a correlation between M_c and M_e definite correspondence can be revealed for small groups of similar polymers.^{50, 51} However, it should be noted that the values of both viscosity at finite concentrations of polymers and their MM exceed critical values and the elasticity moduli in the high-elasticity plateau region

[†] Based on the concepts of classical theory of network elasticity, the chain length between the network entanglements (M_e) may be calculated from the magnitude of the elasticity modulus in this region.^{9, 47, 48}

depend on the size of the polymeric coil. This circumstance was apparently first brought to light by Fox⁵² and this fact was repeatedly confirmed in later studies.^{48, 53, 54} It has been shown that the M_c values for many polymers approximately correspond to one size of the macromolecular coil: the characteristic viscosity $[\eta]_c$ corresponding to the M_c value of different polymers amounts to $\sim 13 \text{ dl g}^{-1}$ (26 polymers were analysed). This conclusion was confirmed by Chee⁵³ (35 polymers) and He and Porter⁵⁴ (37 polymers). The latter study has shown that the mean square radius of the coil of the critical size of a macromolecule $\langle R_c^2 \rangle^{1/2}$ is constant

and equal to about 4 nm (the spread of values from 1.3 nm for poly(oxy-2,6-dimethyl-1,4-phenylene) to 5.9 nm for poly(dodecyl methacrylate).

An illustrative example of the invariance of the coil critical size was given in a study of Baird and Ballman.⁵⁵ The dependence of viscosities of the rigid-chain poly(*p*-phenylene terephthalate) (the persistence length $A = 130 \text{ nm}$, $M_c = 1180$) and the flexible-chain nylon-6,6 ($A = 9.4 \text{ nm}$, $M_c = 5300$) on MM is the same, if not the MM proper but the polymer coil size (characteristic viscosity) is used as the argument. Table 1 contains the values of characteristic

Table 1. Parameters of a macromolecular coil under critical conditions.

Polymer	M_c (see Ref. 49)	$10^4 K\theta / \text{dl g}^{-1}$	$[\eta]_c / \text{dl g}^{-1}$	$\rho / \text{g ml}^{-1}$	$[\eta]_c \rho$	$\langle R^2 \rangle^{1/2} / \text{nm}$
PE	3500 ^a	22.5 ^a	—	0.85 ^a	—	2.67 ^e
PPr	6890	15 ^b	0.125	0.85 ^b	10.6	2.73
PB	—	—	—	—	—	4.73 ^c
PIB	16020	10 ^b	0.127	0.86 ^b	10.9	3.64
<i>cis</i> -PB	5940	17 ^b	0.131	0.92 ^c	12.0	2.64
<i>cis</i> -PI	7650	11.9 ^c	0.104	0.906 ^c	9.4	2.66
PDMS	24500	7.8 ^d	0.122	0.970 ^d	11.0	4.14
PS	35000	8 ^b	0.150	1.06 ^c	15.9	4.99
PVA	24540	8.6 ^d	0.134	1.108 ^d	14.5	4.28
PVC	6250	12.5 ^b	0.099	1.38 ^c	13.7	2.45
PAA	—	—	—	—	—	4.44 ^e
PAM	—	—	—	—	—	2.47 ^e
PAN	1330	22.5 ^b	0.082	1.154 ^c	9.5	1.37
PMMA	31530	6.5 ^b	0.115	1.19 ^c	13.7	4.42
PBMA	60435	2.95 ^c	0.073	1.05 ^c	7.7	4.70
PHMA	91900	4.3 ^c	0.130	1.007 ^b	13.1	6.57
POMA	114000	5.2 ^b	0.062	0.971 ^b	6.0	7.80
PDDMA	18640 ^a	3.5 ^a	—	0.98 ^a	—	5.89 ^e
PEBMA	—	—	—	—	—	3.45 ^e
PEO	4410	13 ^c	0.086	1.13 ^b	9.7	2.08
P- ϵ -CL	5020	25.3 ^c	0.179	0.985 ^d	17.6	2.77
PMA	24100	7.2 ^d	0.112	1.11	12.4	4.80
1,2-PB	4110	12.5 ^d	0.080	0.899	7.2	1.98
PTMO	2530 ^a	23.1 ^a	—	0.98 ^a	—	2.01 ^e
PPO	7750	11.6 ^d	0.102	1.000	10.2	2.98
P- α -MS	40800	7.4 ^c	0.1495	1.04	15.5	5.25
P- <i>p</i> -MS	5010 ^a	6.9 ^a	—	1.04 ^a	—	—
P- <i>m</i> -MS	—	—	—	—	—	4.48 ^e
PTFE	6000 ^b	17.8 ^b	0.14 ^b	—	—	2.69 ^e
	3270 ^a	21.0 ^a	—	1.34 ^a	—	—
PEIP	—	—	—	—	—	1.63 ^e
PETP	—	—	—	—	—	2.50 ^e
PDMP	—	—	—	—	—	1.28 ^e
PC	3000 ^b	21.4 ^b	0.12 ^b	—	—	1.88 ^e
PDeMS	4000 ^b	19.6 ^b	0.12 ^b	—	—	2.54 ^e
PTMA	6000 ^a	19.0 ^a	—	1.02 ^a	—	—
	6000 ^b	19.0 ^b	0.15 ^b	—	—	—
PDeMA	4500 ^b	19.8 ^b	0.13 ^b	—	—	2.53 ^e
PDeS	4000 ^b	20.2 ^b	0.13 ^b	—	—	2.57 ^e
PHMS	—	—	—	—	—	2.55 ^e
PVCz	27100 ^a	7.6 ^a	—	1.19 ^a	—	—
PPS	20 000 ^a	6.0 ^a	—	1.04 ^a	—	—
PVN	14700 ^a	6.5 ^a	—	1.19 ^a	—	—

^aData from Ref. 53; ^bdata from Ref. 48; ^cdata from Ref. 57; ^ddata from Ref. 58; ^edata from Ref. 54.

Note. PE, polyethylene; PPr, polypropylene; PB, poly(1-butene); PIB, polyisobutylene; *cis*-PB, poly(*cis*-1,4-butadiene); *cis*-PI, poly(*cis*-1,4-isoprene); PDMS, polydimethylsiloxane; PS, polystyrene; PVA, poly(vinyl acetate); PVC, poly(vinyl chloride); PAA, poly(acrylic acid); PAM, polyacrylamide; PAN, polyacrylonitrile; PMMA, poly(methyl methacrylate); PBMA, poly(n-butyl methacrylate); PHMA, poly(n-hexyl methacrylate); POMA, poly(n-octyl methacrylate); PDDMA, poly(dodecyl methacrylate); PEBMA, poly(2-ethylbutyl methacrylate); PEO, poly(ethylene oxide); P- ϵ -CL, poly(ϵ -caprolactam); PMA, poly(methyl acrylate); 1,2-PB, poly(1,2-butadiene); PTMO, poly(tetramethylene oxide); PPO, poly(propylene oxide); P- α -MS, poly(α -methylstyrene); P-*p*-MS, poly(*p*-methylstyrene); P-*m*-MS, poly(*m*-methylstyrene); PTFE, polytetrafluoroethylene; PEIP, poly(ethylene isophthalate); PETP, poly(ethylene terephthalate); PDMP, poly(2,6-dimethyl-1,4-phenylene); PC, poly(bisphenol A carbonate); PDeMS, poly(decamethylene succinate); PTMA, poly(tetramethylene adipate); PDeMA, poly(decamethylene adipate); PDeS, poly(decamethylene sebacate); PHMS, poly(hexamethylene sebacate); PVCz, polyvinylcarbazole; PPS, poly(propylene sulfide); PVN, poly(2-vinyl naphthalene).

viscosity $[\eta]_c$ for different polymers. The coil radius was calculated by the Flory–Fox formula⁵⁶

$$\langle R_c^2 \rangle^{1/2} = \frac{([\eta]_0 M_c)^{1/3}}{\Phi},$$

where $[\eta]_c$ is the characteristic viscosity of the θ -coil and $\Phi = 2.87 \times 10^{21}$. It is seen that the values of the critical radii of the coils of different polymers are close.

Antonietti *et al.*⁵⁹ have shown that macromolecules of polystyrene with different topologies (linear, cyclic and star-like with different numbers of branches and microgel spheres) also exhibit the same dependence of viscosity on MM if the argument is the polymer coil size. An analogous result was also obtained for other types of polymers, *viz.*, rigid-chain,⁶⁰ liquid-crystalline,⁶¹ comb-shaped,⁶² and branched^{63,64} ones. The use of characteristic viscosity allows unification of the data on viscosity of different polymer systems over a wide concentration range.⁶⁵

Such a similarity of the behaviour of macromolecules (including highly cross-linked globules) which differ greatly in their nature and topological type is often interpreted from a purely geometrical viewpoint: entanglements can arise only when the coils overlap, *i.e.*, when the total volume of coils (the product of the coils concentration by the macromolecular coil volume) is larger than the system's volume. The criterion ratios proposed by different authors^{49, 52–54, 66, 67} differ in minor details. However, the fact that dense globules⁵⁹ and rigid rods⁶⁰ obey the same regularity casts doubts on the validity of the topological approach.

The data on the correlation between the elasticity moduli G_e in the high-elasticity plateau region and the molecular characteristics of block polymers have been analysed.^{13, 49, 54, 57, 68} The value of

the effective volume of the network of entanglements $([\eta]_0)^\ddagger$ was found to be constant irrespective of the magnitude of M_c , which is determined by the nature (rigidity) of a polymeric chain (Table 2). However, the product $[\eta]_0 \rho$ is somewhat smaller ($\sim 8 \text{ cm}^3 \text{ g}^{-1}$, on the average, for the polymers studied) than that derived from viscosimetric measurements ($13 \text{ cm}^3 \text{ g}^{-1}$). At the first glance, this result does not contradict the simple network model according to which

$$M_c = 2M_e.$$

However, it should be noted that the same regularities are characteristic of both rigid rods⁶⁰ and dense highly cross-linked globules⁵⁹ as well as latex dispersions,⁶⁹ *viz.*, at definite concentrations and/or MM of polymers, the polymeric systems exhibit viscoelastic properties. Evidently, the elastic properties are determined by the network structure resulting from intermolecular interactions which are apparently of an energetic nature.^{61, 70} The viscoelastic properties of comb-like polymers are presumed to be also determined by intermolecular interactions due to the side groups.

IV. Regularities of viscous flow

It is believed that the viscosities of polymers strongly depend on MM ($MM > M_c$) and concentration of the polymers (exponents of 3.4 and ~ 5 , respectively) and are determined by the formation of interchain topological nodes called entanglements (*see, e.g.*, Refs 9, 10, 12–14, 16–19, 46, 71). The entanglements arise in the concentration region where mutual penetration of polymer coils resulting in a cooperative flow of polymer chains occurs. It is presumed^{10, 12, 13} that in the frame of the reptation model, the translation diffusion of polymer chains during such a flow is restricted by the 'tube', *i.e.*, it becomes substantially anisotropic.

Changes in the size of a macromolecular coil upon concentration of a solution are highly important in the studies of the dependence of the viscosity of a polymer solution on the concentration and MM of this polymer. The dependence of the size of a macromolecular coil on the polymer concentration in the range of semidilute and concentrated solutions was investigated both theoretically^{10, 13, 72, 73} and experimentally.^{74–76} Flory⁷⁷ was the first to notice that the coil changes its dimensions upon transition from dilute to concentrated solutions. In the isolated state (in a dilute solution), the conformation of macromolecules is determined by the competition of two factors, *viz.*, the effect of excluded volume and the energy of interaction of monomeric units with the medium (in an athermal solution where the interaction energy does not play any role and the coil swells owing to the effect of excluded volume), while, according to Flory, the coil should have the θ -dimensions in the bulk.

Edwards *et al.*^{13, 73} proposed a theory based on the idea of screening of the energy of repulsion of monomeric units of the same chain by the units of the neighbouring chains. With such a screening, the effect of excluded volume is neutralised: as in the case of dilute solutions, the energy of repulsion of monomers of the same chain is compensated by the energy of their attraction owing to the interaction with the monomeric units of the neighbouring chains. In this case, the principal role is played by the entropy factor the nature of which has been clearly explained by de Gennes in a simple example.¹⁰ The entropic nature of this factor is manifested in that the temperature factor influences the size of the θ -coil in a melt to a substantially lesser extent than in a dilute solution.⁷⁸

For the same reason, the concentration dependences of the swelling coefficient shown in Fig. 1 comprise two regions: in the first region, the shape of the curve is substantially dependent on the nature of the solvent and the curve may be monotonic or have

Table 2. Characteristics of the chains of a network of entanglements.

Polymer	M_c	$[\eta]_0 / \text{cm}^3 \text{ g}^{-1}$	$[\eta]_0 \rho$
PE	828 ^a	6.47	5.1
PEO	1624 ^a	5.24	5.6
PPr	4623 ^a	10.20	8.0
PMMA	10013 ^a	6.50	7.4
PS	13309 ^a	9.23	8.9
PDMS	12293 ^a	8.60	7.7
<i>cis-trans</i> -PB	2300 ^b	9.8	—
<i>cis-trans</i> -PI	3900 ^b	9.9	—
PEB	5500 ^b	9.6	—
PPB	8000 ^b	9.8	—
PBB	10800 ^b	10.2	—
PIPB	8000 ^b	9.8	—
PIBB	1080 ^b	10.2	—
<i>cis</i> -PB	3500 ^b	10.1	9.3
<i>cis</i> -PI	4500 ^b	8.7	7.9
PMB	4400 ^b	10.5	—
PP	3600 ^b	10.0	—
SKS-25	3450 ^b	10.4	—
BPR	2400 ^b	10.1	—
EPR	2100 ^b	8.9	—
SKF-260	6200 ^b	8.7	—
SKF-260 MP	10500 ^b	6.15	—
PPO	4500 ^b	7.8	7.8
PTMO	2000 ^b	10.3	10.1
PIB	8000 ^b	10.2	8.8

^aData from Ref. 57; ^bdata from Ref. 68.

Note. PEB, polyethylbutadiene; PPB, polypropylbutadiene; PBB, polybutylbutadiene; PIPB, polyisopropylbutadiene; PIBB, polyisobutylbutadiene; PMB, polymethylbutadiene; PP, polypiperylene; BPR, butadiene–propylene rubber; EPR, ethylene–propylene rubber; SKS-25, SKF-260 and SKF-260 MP, synthetic rubber brands.

[‡] As in this case one deals with the bulk polymers, the macromolecular coil has the θ -dimensions.

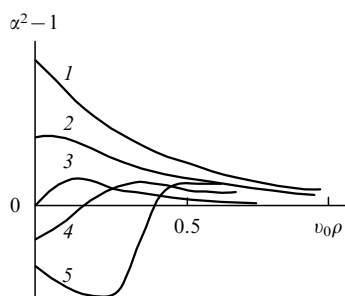


Figure 1. Dependence of the swelling coefficient α on the concentration of polymer segments ρ in a solution at different temperatures (differing solvent quality).⁷²

$(1 - \theta/T)N$: (1) > 0.75 , (2) 0.75 , (3) 0 ; $(1 - \theta/T)N$: (4) < 0.75 , (5) > 0.75 . v_0 , segment volume; θ , Flory temperature; N , chain length.

extrema (the region of dilute solutions); in the second region, the shape of the curve is the same for solvents of any type.

Variation of the size of a macromolecular coil as a function of the polymer solution concentration is described by power dependences, for example:¹³

$$\frac{\langle R^2 \rangle}{\langle R^2 \rangle_0} - 1 \propto c^{1/2} \text{ or } R_g = R_g^0 \left(\frac{c}{c^*} \right)^{2\nu-1/2(1-3\nu)},$$

where R_g is the hydrodynamic radius of the polymer coil, c^* is the critical concentration (the boundary between dilute and semidilute solutions), ν is the power index in the relation

$$\langle R^2 \rangle^{1/2} \propto M^\nu,$$

where M is the molecular mass of a polymer.

Usually, experimental data are also presented in the form of power dependences.^{74, 79}

It should be noted that the above dependences can serve as estimates. As is mentioned in the monograph of Doi and Edwards,¹³ 'the scaling argumentation gives only a qualitative picture of the dependence on basic parameters'.

The sought dependence of the macromolecular coil size on the polymer concentration may be derived by analysing computer simulation models.^{79–81} As a rule, these models take into consideration only the factor of the excluded volume, *i.e.*, the repulsive part of the interaction potential. This means that the computer simulation techniques investigate athermal systems.

The results of such simulations indicate^{79, 80–82} that the following simple relation is obeyed over the entire concentration range (Fig. 2a).

$$\frac{V_c}{V_0} = \frac{1}{1 + \gamma c}, \quad (3)$$

where V_c and V_0 are the coil volumes at the concentration c and in an extremely dilute solution, respectively; γ is a coefficient.

The coefficient γ depends on the chain length N (Fig. 3)

$$\gamma = N^a,$$

where the exponent a is equal to 1 for short chains and $a \simeq 0.34$ for long chains. Such a character of the dependence may be explained qualitatively by the relationship between the coil size and the length of the chain contour: the linear dependence in the first case and the exponential dependence with the exponent $1/2$ in the second case.

The validity of relation (3) is illustrated in the experiments showing the effect of 'thickening' (increase in concentration) of a polymer solution on the diffusion of macromolecular coils,⁸³ viscosity^{2, 84, 85} and characteristic viscosity of the polymer.^{86–90} For corresponding analysis of the experimental results, see Ref. 82.

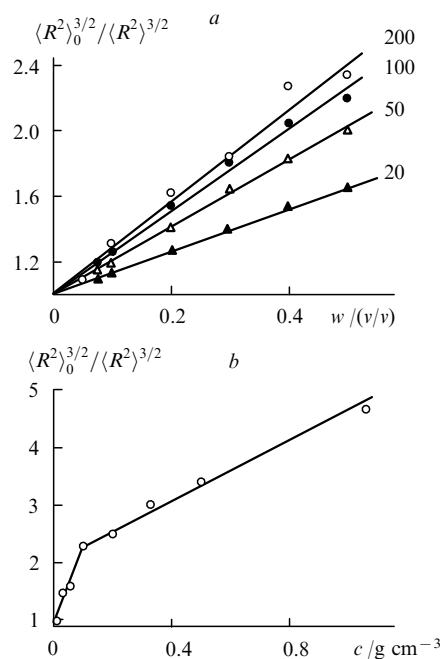


Figure 2. Dependence of the size of a macromolecular coil on the polymer concentration in the coordinates of Eqn (3); (a), data from computer simulation,⁸¹ the numerals at the straight lines indicate the chain length; (b), system PS – carbon disulfide.⁷⁴

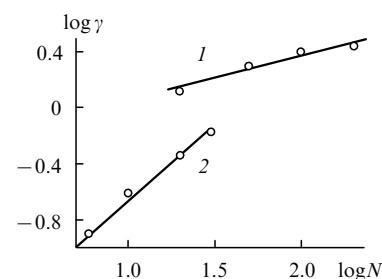


Figure 3. Dependence of the coefficient γ from Eqn (3) on the chain length according to the data reported by de Vos and Bellemans⁷⁹ (1) and Paul *et al.*⁸¹ (2).

By comparing changes in the diffusion coefficients of a rigid sphere (chloroform as the solvent) and a macromolecular PS coil (toluene as the solvent) upon concentration of solutions in the PMMA concentration range from 0% to 5%, Brown and Rymden⁸³ have concluded that the size of the coil of the PS macromolecule depends on the 'thickener' concentration. As the molecular masses of PS and PMMA are high (ranging from 1.26×10^6 to 15×10^6 for the former and from 1.01×10^5 to 4.45×10^5 for the latter), the solutions in the above-mentioned concentration range are regarded, if not as concentrated, at least as semidilute ones for which the entropy factor is decisive.

In the experiments⁸⁶ on measuring the characteristic viscosity of PS ($MM = 3.5 \times 10^6$) in a mixture of bromoform with PS with $MM = 0.46 \times 10^5$ or PS with $MM = 1.1 \times 10^6$ as the 'thickener', the interval of the system's volume 'packing' {parameter $[\eta]c$ } is overlapped almost 10 times which is undoubtedly indicative of the transition to the region of concentrated solutions.

The results of the studies on the variation of the coil size as a function of concentration of polymers obtained by the neutron scattering method (Fig. 2b)⁷⁴ are not described by relation (3). Possibly, in this system the break in the straight line corresponds to the critical concentration of transition from a dilute solution to semidilute one, *i.e.*, the energy factor plays the decisive role in the initial stage. Daud *et al.*⁷⁴ used carbon disulfide which is a good

solvent. There are no accurate data on the characteristic viscosity of PS in this solvent, although it may be assessed using the Mark–Kuhn equation

$$[\eta] = KM^a;$$

if it is assumed that $K = 1 \times 10^{-4} \text{ dl g}^{-1}$ and $a = 0.72$,⁵⁸ then $[\eta] = 0.44 \text{ dl g}^{-1}$, while the critical concentration is $\sim 0.02 \text{ g ml}^{-1}$. Of course, these values are lower than the value of characteristic viscosity corresponding to the inflection point on the graph, though they are close in their orders of magnitude.

It is also possible that a definite role in the above discrepancy is played by some additional factors, *e.g.*, the sample prehistory.⁹¹

Thus, the analysis of experimental data and results of computer simulation make it possible to conclude that formula (3) may be used for the description of the concentration dependence of the coil size in the range of semidilute and concentrated solutions of polymers.

It is noteworthy that relation (3) is a consequence of the dependence established for dilute solutions^{84,85}

$$V_c = V_0(1 - \gamma[\eta]c + \dots). \quad (4)$$

For low concentrations of polymers

$$V_c - V_0 = -kV_0^2c, \quad (5)$$

since

$$[\eta] \propto V_0.$$

If the latter expression is assumed to hold for finite values of concentration c , then Eqn (5) may be presented in form of the differential equation

$$dV = -kV^2dc, \quad (6)$$

from which Eqn (3) is derived by integration. It is seen that the coefficient

$$\gamma = kV_0$$

is a function of MM.

The fact that the principal quantity in Eqn (3) is the product $[\eta]c$ means that the scaling relations are virtually fulfilled,^{10,13} *i.e.*, the macromolecular coil size depends on the dimensionless parameter c/c^* .

Equation (6) is valid over the entire range of concentrations for both dilute and concentrated solutions of polymers (the differing k values, see Fig. 2*b*). This means that a polymeric solution of any concentration acts as a continuous medium for a macromolecular coil and that there is no difference in principle between the solvent and the polymer solution: the difference is purely quantitative due to different energetic interaction of the polymer chain with the medium and viscosity, which is confirmed by diffusion experiments.⁸³

This may also mean that macromolecular coils behave independently during the flow of a polymeric solution and/or a melt *viz.*, interactions of the entanglement type do not affect the viscosity. In other words, Eqn (3) holds over the entire range of polymer concentrations (up to its melt).

This hypothesis formed the basis for the analysis of the viscosity dependence on the concentration and MM of a polymer.^{2,92–95} It turned out that over a certain concentration interval depending on the glass transition temperature of a system, all polymers obey the following law:

$$\ln \eta_{\text{rel}} = K^{-1} \ln[1 + K[\eta]_c(c - c^*)], \quad (7)$$

where $\eta_{\text{rel}} = \eta/\eta_c$, η_c is the viscosity of a polymer solution at the critical point, $[\eta]_c$ is the characteristic viscosity of a polymer at the critical point, $K = 0.125$ for all the polymers studied.

As an example, Fig. 4 shows the data on the viscosity of polydimethylsiloxane solutions in siloxane pentamer.⁹⁶ The curves plotted in the coordinates of Eqn (7) are straightened over the entire range of concentrations and MM, the straight line slope {the product $K[\eta]_c$ } being dependent on MM in conformity with

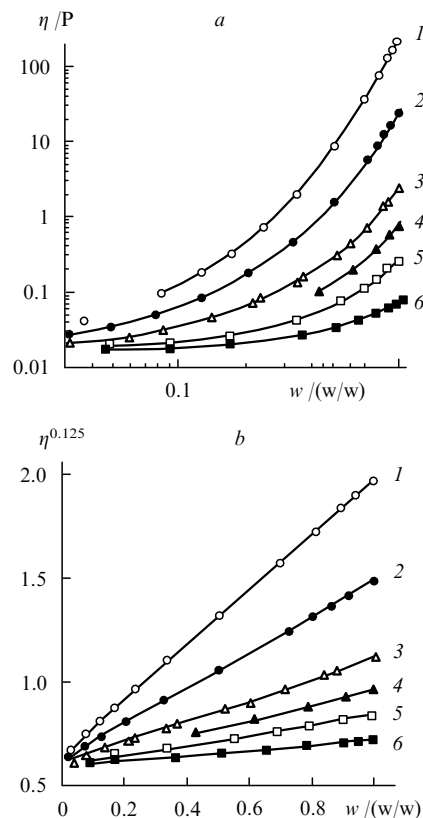


Figure 4. Dependence of the viscosity of polymethylsiloxane on its MM and concentration in the siloxane oligomer with the chain length equal to 5 plotted in the logarithmic coordinates (*a*) and the coordinates of Eqn (7) (*b*);⁹⁶ $10^3 M_w$: (1) 490; (2) 152; (3) 88; (4) 36; (5) 11.2; (6) 2.9.

the Mark–Kuhn equation. In this case, the exponent a is equal to 0.54, which is somewhat larger than under θ -conditions but smaller than in an athermal solution. Analogous conclusions have been drawn from other studies.^{89,94} The corresponding data are listed in Table 3.

According to the data reported by Kataoka and Ueda,⁹⁶ the M_c of the bulk polymer is 27 000 (30 000, according to Ref. 48). However, there is no kink in the dependence of viscosity on MM plotted in the coordinates of Eqn (7) (Fig. 5*a*). Naturally, such a kink will certainly be absent at lower polymer concentrations.

The results obtained may be suggested to be due to that the polysiloxane fractions had a broad molecular-mass distribution ($\overline{M}_w/\overline{M}_n \approx 2$). However, the data on the viscosity of PS⁵⁹ with a rather narrow molecular-mass distribution ($\overline{M}_w/\overline{M}_n \geq 1.1$) and of polybutadienes¹⁰² also with a narrow molecular-mass distribution over a very wide MM range (from 10^3 to 10^7) point to the preservation of the above regularity (Fig. 5*b*). The linear law

Table 3. Parameters of the Mark–Kuhn equation for the critical point.⁹⁴

Polymer	$10^4 K / \text{dl g}^{-1}$	a	Ref. ^c
PDMS	5.8	0.54	96
PIB ^a	9.7	0.50	97
PIB ^b	—	0.53	98
PVA	2.95	0.56	99
PVC	3.2	0.66	100
P- α -MS	—	0.4	101

^a Solvent, xylene. ^b Solvent, carbon tetrachloride. ^c The references comprise the studies the results of which were used to calculate parameters of the Mark–Kuhn equation.

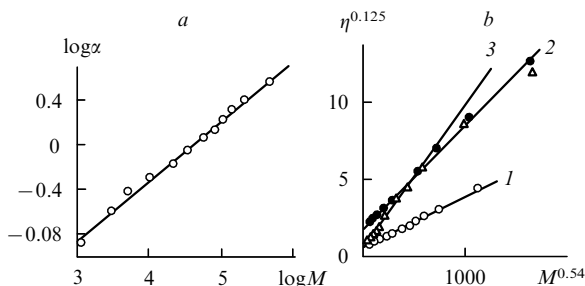


Figure 5. Dependence of Eqn (7) parameters on MM of polydimethylsiloxane⁹⁶ (a) and bulk polydimethylsiloxane⁹⁶ (1), PE⁵⁹ (2) and polybutadiene¹⁰² (3) (b); α is the slope of the straight lines in Fig. 4b.

holds up to MM of the order of 10^6 . Deviation from the linearity observed for samples with larger MM may be due to their higher polydispersity. It should be noted that an analogous deviation from linearity is observed in double logarithmic coordinates.

The conclusion about the independence of macromolecular coils in concentrated solutions was confirmed by the data on the relationship between the solution viscosity and the longest relaxation time (τ) determined from the critical gradient rate in the longitudinal flow of solution between two coaxial capillaries.⁸⁷ It was shown that the following relation holds over a wide range of polymer concentrations

$$\tau = A \frac{M[\eta]\eta_0}{RT},$$

where A is a coefficient and η_0 is the solvent viscosity. In this equation which is valid for dilute solutions,⁵⁶ the role of the solvent viscosity is played by the solution viscosity.

The above results make it possible to conclude that the critical conditions under which a kink in the plot of the viscosity dependence on MM and concentration of a polymer is observed, are not associated with the transition of the individual flow of coils into a cooperative one. This artefact is determined by the representation of the sum of two magnitudes in logarithmic coordinates [see Eqn (7)].

Apparently, the reptative character of the displacement of chains in the flow of polymer solutions is manifested at the MM and concentrations of polymers which are appreciably larger than the critical ones. Thus it was suggested that¹³ the true reptation manifests itself in the range of MM of about $800 M_c$, i.e., the values of the order of tens of millions.

V. Diffusion of macromolecules

Various aspects of the translational diffusion of polymers have been reviewed by Green.²⁰ In experiments, the criterion of transition from the R-dynamics to the reptation dynamics was the dependence of the diffusion coefficient on the molecular mass of the chain, which is linear in the R-model and quadratic in the reptation model. Various methods (ranging from radioactive labelling NMR spectroscopy) and different polymers (PS, PE, PDMS, etc.) were used for deriving quantitative data. Having analysed the available experimental results concerning the diffusion of polymers in bulk and in mixtures, Green²⁰ concluded that the diffusion coefficient depends on the mixture composition, the dependence being often non-monotonic.

In many cases, the validity of the dependence characteristic of the reptation mechanism was revealed.

$$D \propto M^{-a},$$

where $a = 2$. It should however be emphasised that in the graphs plotted from the results of Green's study²⁰ all the points fall onto the same straight line for both $MM > M_c$ and $MM < M_c$. At the same time, this author points to numerous data which show that

the exponent a for the polymers with MM substantially higher than M_c is markedly smaller than 2 (e.g., for PDMS¹⁰³). In the case of polyisoprene,²⁰ this exponent is, on the contrary, close to 3, while in the 60% solution of PS in dibutyl phthalate¹⁰⁴ $a = 2.6 \pm 0.2$. Comparative investigation of the dependences of viscosity and diffusion of hydrogenated polybutadiene has been carried out by Pearson *et al.*,¹⁰⁵ who have shown that at the MM much higher than M_e ($MM > 9M_e$) the following relation is respected

$$(D\eta)_{\text{rep}} = (D\eta)_R \left(\frac{M}{M_e} \right),$$

where the subscripts 'rep' and 'R' denote the reptation and Rouse models, respectively.

Similar results were obtained for PS and hydrogenated polyisoprene. It was proposed to describe diffusion in the general form using the expression

$$D\eta = (D\eta)_{\text{rep}} + (D\eta)_R = (D\eta)_R \left[1 + \left(\frac{M}{M^*} \right)^d \right],$$

where $M^* = (9.5 \pm 1.1)M_e$ and $d = 1.5 \pm 0.1$.

In order to describe the dependence of diffusion coefficient on MM and concentration of a polymer, more complex expressions are used, in particular the 'stretched' exponent:^{106, 107}

$$D \propto \exp(-kM^b),$$

where $b = 1$ for low MM and $b < 1$ for high MM. Such a character of the dependence is related¹⁰⁸ to the Kohlrausch–Williams–Watts law.¹⁰⁹ This expression is empirical but this does not prevent its use because the power dependences fit experimental results poorly. Indeed, the results reported by Pahl *et al.*¹¹⁰ indicate that the dependence of the diffusion coefficient of PDMS (with MM ranging from 118 000 to 716 000) on MM is an exponential function rather than a power one. These investigators revealed a trend towards the transition of the translational diffusion to the reptation regime; however, the reptation regime was not achieved because of the time limit (~ 1 s, with the use of NMR in a gradient field).¹¹⁰

Experimental studies of diffusion were carried out in dilute and semidilute solutions of polymers using different methods, in particular NMR spectroscopy in a gradient field,^{22, 29, 111, 112} dynamic light scattering¹¹³ and neutron spin echo.^{23, 114}

The dependence of dynamic (including also diffusive) characteristics of macromolecules on the solution concentration is determined by the characteristic parameter ξ , viz., the correlational length of the excluded volume.^{10, 13} The dependence of this parameter on concentration, for example, for a semidilute solution is as follows:

$$\xi \propto c^{-v/(3v-1)} \propto c^{-3/4}.$$

With the consideration of this formula, the diffusion coefficient of a polymeric chain in the range of concentrations corresponding to semidilute solutions is expressed as

$$D \propto N^{-2} c^{-1.75}.$$

As noted above, experimental results are more likely to indicate an exponential function.^{106, 107, 115} Thus depending on the nature of the solvent and the polymer, the value of power v in the 'stretched' exponent varied from 0.42 to 2.21.¹¹⁵ In addition, v depends on MM

$$v \propto M^{-0.25}$$

as results from the analysis of more than 40 systems show.

The validity of specific models is confirmed by the results of computer simulation of the dynamics of polymers^{116, 117} using molecular dynamics^{30, 32} and Monte Carlo methods.^{118–124}

Despite its somewhat artificial character, the Monte Carlo method is often used in studies of physical properties of polymers,³¹ and it was this method that provided basic information on the dynamics of macromolecules. As the investigation of dense

(bulk) systems by computer simulation techniques is a rather complex problem, the concentration factor was found to play a substantial role: basic results were obtained for the systems in which the polymer concentrations did not exceed 50%.

With the Monte Carlo method, the main attention is paid to the investigation of the dependence of the chain diffusion coefficient on the concentration and MM.¹¹⁸ In this context, the following trends have been brought to light:

(i) as the concentration increases, the power index a in the dependence of maximum relaxation time τ on MM

$$\tau \propto N^a$$

varies from 2 to 3, which corresponds to the change in the conditions of chain displacement, *i.e.*, from the R-regime to the reptation regime;

(ii) at low concentrations, the temporal dependence of the displacement of the macromolecule mass-centre obeys the relation

$$g_m \propto t^{0.54};$$

(iii) as the concentration increases, the power index approaches 0.50, which is related to the above-discussed compression of the polymer coil to the θ -dimensions;

(iv) the squared shear of the inner monomeric chain depends over some time interval on the current time (t)

$$g_m \propto t^{0.3},$$

which is interpreted as manifestation of the reptation mechanism in which the power index should be equal to 0.25.

It should be noted that the extension of the results obtained to the range of polymer concentrations close to 100% leads to a paradoxical conclusion that the dependences of diffusion coefficient and maximum relaxation time on MM become stronger than those predicted by the reptation model: the power indexes increase to 2.4 and 3.6, respectively.¹²⁰ Furthermore, restriction of the lateral shift of the segregated chain was revealed solely in the case on 'frozen' environments. If in a mobile system, all chains are equally mobile, the 'tube' effect, expressed in the anisotropy of the differentiated chain motion, is not manifested.

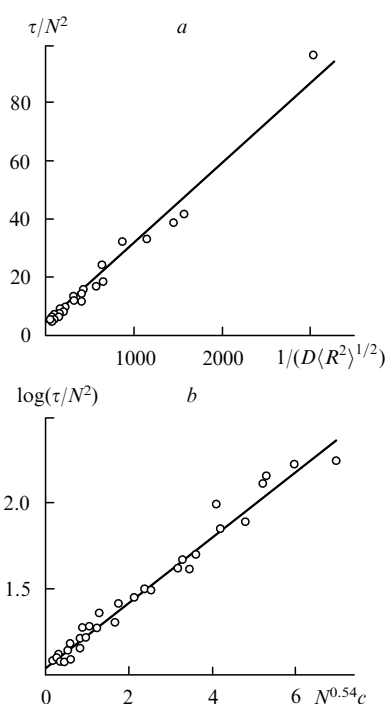


Figure 6. Dependence of the minimum time of R-relaxation τ/N^2 on the macromolecule size:^{81, 119} (a) in the Stokes equation coordinates; (b) concentration dependence.

On the other hand, the analysis of the dependences of the diffusion coefficient D and maximum relaxation time τ reported by Paul *et al.*^{81, 119} shows that the relationship between τ and D^{-1} is linear over the entire range of concentrations studied for all lengths of chains and for all lengths of chains except for 20 (*i.e.*, 50, 80, 100, 200), a single dependence has been established (Fig. 6 a)

$$\frac{\tau}{N^2} = \frac{2.6 + 0.027}{D\langle R^2 \rangle^{1/2}}.$$

This formula expresses essentially the Stokes law in which the minimum time of R-relaxation τ/N^2 plays the role of viscosity, whereas the concentration is implicitly accounted for in the values of τ and $\langle R^2 \rangle$. Here, the minimum relaxation time⁸ should not depend on the concentration and MM of a polymer due to the effect of hydrodynamic screening.¹³ However, as one can see from the data shown in Fig. 6 b, such a dependence does exist: the minimum relaxation time is functionally related to the length of the polymeric chain and its solution concentration. It should be emphasised that the dependences observed are linear in the corresponding coordinates and that they have no kinks, which could suggest the transition from the R-mode of relaxation to the reptation regime. Consequently, as in the case of maximum viscosity, cooperativity is not manifested in slow processes of macromolecular diffusion.

VI. Stress relaxation

In the curves of the stress relaxation of linear polymers with a narrow molecular-mass distribution, one can differentiate several zones corresponding to different states of the system:¹²⁵ glassy, transient, highly elastic (plateau of high elasticity) and terminal states (see, *e.g.*, Fig. 7 a). It is seen that MM has no effect on the shape of relaxation curves in the glassy and transient states, this effect being manifested only at the end of the high-elasticity plateau, *viz.*, in the terminal zone. This fact is well known. The high-elasticity modulus exhibits rather small variation in the plateau region. A drastic drop of this modulus (by 90% and

§ This magnitude corresponds to the friction coefficient of a bead of the R-chain. According to the R-model, the polymeric chain is a system of beads (friction elements) connected by elastic elements.

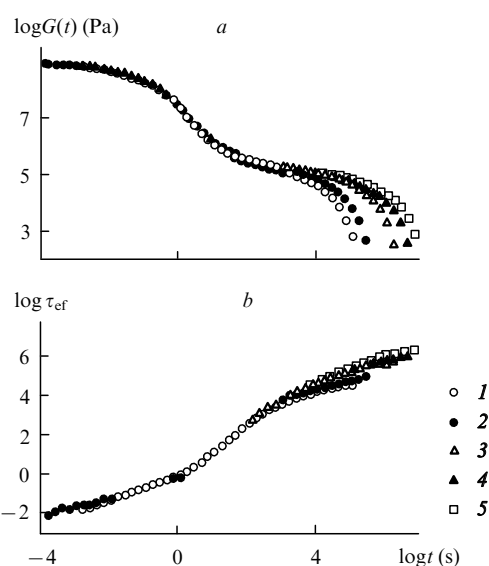


Figure 7. Curves of relaxation of the stress of PS with a narrow molecular-mass distribution;¹²⁶ (a) elasticity modulus; (b) effective time of relaxation; $10^{-3}M$: (1) 80; (2) 125; (3) 193; (4) 239; (5) 267.

more) occurs in the terminal zone, and the kinetics of its decrease strictly obeys the exponential law.

All the zones corresponding to the above-listed ranges are clearly seen in the curves of the dependence of effective relaxation time τ_{ef} on the current time (Fig. 7b)¹²⁶

$$\tau_{\text{ef}} = - \left(\frac{d \ln G(t)}{dt} \right)^{-1}. \quad (8)$$

The relaxation time is approximately proportional to the square root of the time in the region of the transient state, this dependence is almost linear (the power index is slightly larger than 1) in the high-viscosity region, then it weakens in the region where MM begins to have its effect and, finally, the relaxation time becomes invariant with time, *i.e.*, $\tau_{\text{ef}} = \tau_{\text{max}}$.

The data reported by other investigators^{127–129} confirm the above-noted regularities of changes in the stress relaxation. The maximum time of relaxation is MM-dependent (Fig. 8)

$$\tau_{\text{max}} \propto M^4.$$

However, this law cannot always be revealed. Indeed, as is seen from the data shown, on the one hand, if the MM interval is not too large, the regularity may be distorted. On the other hand, relaxation measurements of polymers in a wide MM range are usually performed at strongly differing temperatures, and the use of the temperature–time superposition principle reduces them to a certain selected temperature. Minor inaccuracies in such normalisation may lead to some errors (Fig. 8). The analysis of the whole body of available data provides evidence that it is the above-mentioned law that is observed.

Let us emphasise that the data shown in Figs 7 and 8 refer to polymers with a narrow molecular-mass distribution; therefore, the peculiarities of the stress relaxation noted above are characterised namely by the dependence on the chain length.

It is presumed that the relaxation of relatively short chains is well described by the R-model, while the relaxation of fairly long chains is fitted by the Doi–Edwards (DE) model. Herewith, the R-relaxation occurs in a small segment of the transient zone, which adjoins the high-elasticity plateau and is characterised by the exponential dependence of relaxation on the current time with the exponent 1/2.¹³ However, a thorough analysis¹³⁰ of the shape of the relaxation curves corresponding to the R- and DE-models has shown (Figs 9 and 10) that one can differentiate three segments (in the logarithmic coordinates) in the dependence of the elasticity modulus relaxation on time

$$\frac{G(t)}{G(0)} = \frac{1}{n} \sum_{p=1}^n \exp \left(- \frac{p^2 t}{\tau_{\text{max}}} \right), \quad (9)$$

where

$$G(0) = \frac{6n}{\pi^2 \tau_{\text{max}}} \left(\int_0^\infty G(t) dt \right)^{-1} \quad (10)$$

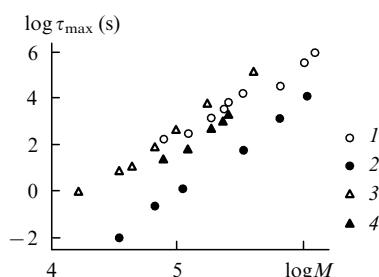


Figure 8. Dependence of the maximum relaxation time on MM of PE according to the data of Akovali¹²⁷ (1), McGrory and Tuminello¹²⁸ (2), Lin¹²⁹ (3) and Aklonis and Tobolsky¹²⁶ (4). Normalised temperature/°C: (1 and 4) 129; (2) 160; (3) 127.5.

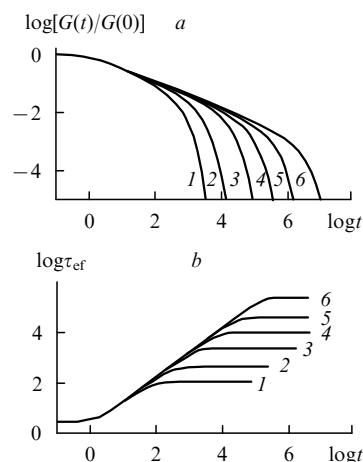


Figure 9. Curves of the stress relaxation (a) and the temporal dependence of the effective time of R-relaxation (b) according to Eqns (8)–(10). The chain length: (1) 11; (2) 21; (3) 51; (4) 101; (5) 201; (6) 501.

where τ_{max} is the maximum relaxation time and n is the R-chain length.

These are

(i) the linear segment for the interval of relative relaxation $\sim 0.9 < G(t)/G(0) < 1$ and $t/\tau_0 \leq 1$ (τ_0 is the minimum time of R-relaxation);

(ii) the segment of the power dependence with the power index 1/2 for the interval $0.1 < G(t)/G(0) < 0.9$ (depending on the chain length, the left limit may be smaller)

$$\frac{G(t)}{G(0)} \propto \left(\frac{t}{\tau_0} \right)^{-1/2},$$

this relaxation interval corresponds to the time t of variation of the relaxation time from its minimum to maximum value;

(iii) the segment of the exponential decay of the relaxation modulus

$$\frac{G(t)}{G(0)} \cong \frac{1}{n} e^{-t/\tau}.$$

This segment of the curve corresponds to the region in which the elasticity modulus amounts to fractions of a percent of the initial value, while the time t is longer than the maximum relaxation time: $t/\tau_{\text{max}} > 1$.

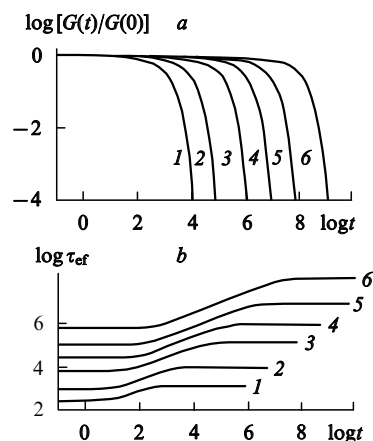


Figure 10. Curves of the stress relaxation (a) and the temporal dependence of the effective time of DE-relaxation (b) according to Eqns (8), (11) and (12). The chain length: (1) 11; (2) 21; (3) 51; (4) 101; (5) 201; (6) 501.

Characteristically, regardless of the time, each of the relaxation curve segments refers to a strictly definite range of values of the relaxation degree $G(t)/G(0)$. Thus the criterion of R-relaxation may be the observance of the power law with the power index equal to 1/2 in the region of the degree of relaxation 0.8–0.1. The interval corresponding to this relaxation is the longer the higher is the MM of a polymer, which is also inherent in the R-model.

It is also typical that the dependence of the effective time of R-relaxation on time τ_{ef} proves to be proportional to time, namely, in the wide range (where the elasticity modulus decreases proportionally to the square root of the time) (see Fig. 9b). According to the R-model,

$$\tau_{\text{max}} \propto M^2.$$

According to the DE-model, temporal changes in the relaxation modulus obeying the relations

$$\frac{G(t)}{G(0)} = \frac{8}{\pi^2} \sum_{p=1,3,\dots}^n p^{-2} \exp\left(-\frac{p^2 t}{\tau}\right), \quad (11)$$

$$G(0) = \frac{12}{\pi^2 \tau} \left(\int_0^\infty G(t) dt \right)^{-1}, \quad (12)$$

are characterised by substantially farther extension of the region of high-elasticity plateau than in the R-model (Fig. 10). In this case, the drop of the modulus in the plateau region is insignificant (see Fig. 10a). The plateau passes smoothly to the exponential decay; the transition interval is rather narrow, while its position in the time scale depends on MM.

The temporal dependence of the effective time of DE-relaxation has its characteristic features, too (Fig. 10b). In the R-model, the minimum value of τ_{ef} is independent of MM and its maximum value is proportional to the square of MM, whereas in the DE-model the minimum and maximum values of τ_{ef} are proportional to the square and the cube of MM, respectively.

The temporal dependence of the effective relaxation time in the transient range obeys the law

$$\tau_{\text{ef}} \propto t^{1/2}.$$

Comparison of the features of the relaxation curves corresponding to the models considered with experimental results shows that none of these models fit the experimental results.

According to the experimental data, the elasticity modulus decreases by $\sim 30\%$ in the region of high-elasticity plateau, whereas the models studied suggest a substantially smaller drop, particularly in the case of the DE-model.

The experimental curves of relaxation comprise no segment corresponding to the exponential dependence with the power index 1/2, which contradicts the R-model. A segment of the exponential dependence of τ_{ef} on t , which may be ascribed to the DE-relaxation, can be found only in individual curves in the transient range (transition from the plateau to the exponential drop) (see, e.g., curve 5 in Fig. 7b). Though, such a segment is virtually absent on the curves describing the relaxation of PS over a wider MM interval. However, one cannot assume that the high-elasticity plateau corresponds totally to the R-relaxation for the following reasons. Firstly, the dependence of τ_{ef} on t is non-linear: in the logarithmic coordinates, $\tan \alpha > 1$ (~ 1.3) in the maximum dependence region. Secondly, as noted above, in the R-relaxation the segment corresponding to the transient state covers a considerable interval of the relaxation degree which is the longer the larger is the MM. In the experimental curves, this segment is little dependent on the chain length and covers the range of $\sim 90\%$ relaxation, which, of course, is substantially more than follows from the DE-model. Finally, the dependence of the maximum relaxation time on MM is a function with the exponent 4 and is not a quadratic function as in the case of R-relaxation, nor is it a cubic function as in the case of reptation model.

The frequency (ω is the frequency of impact) dependence of the relaxation of the real and imaginary parts of the elasticity modulus for narrow PS fractions is shown in Fig. 11.¹³¹ The corresponding dependences for the R- and DE-models are presented in Figs 12 and 13. It is seen that the relaxation curves cannot be described by any of the models discussed. Thus the curve reflecting the frequency dependence of the relaxation of the real part of the elasticity modulus has virtually no segment of exponential dependence with the exponent 1/2 characteristic of the R-model. However, in contrast to the curves typical of the DE-model, the experimental curves exhibit a substantial decay (by almost one order of magnitude) of the elasticity modulus in the region of the high-elasticity plateau.

The decrease in the imaginary part of the elasticity modulus in the high-frequency region occurs much more slowly than those predicted by the R- and DE-models: the power index in the dependence of elasticity modulus relaxation is equal to 1 for the

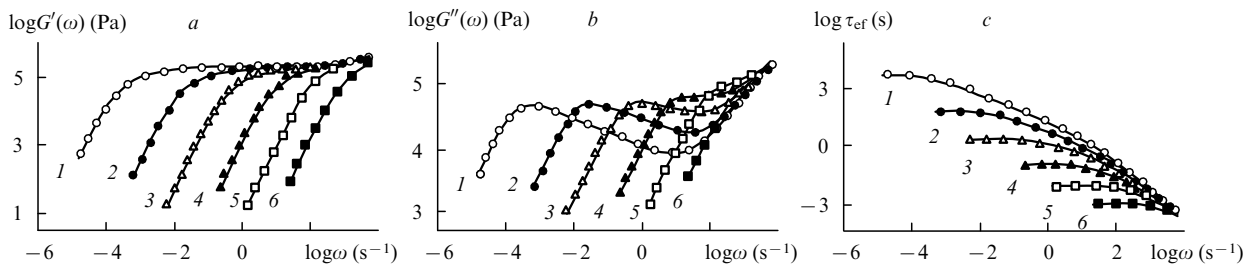


Figure 11. Frequency dependences of the real (a) and imaginary (b) parts of the elasticity modulus and of the effective time of PS relaxation (c).¹³¹ $10^{-3}M$: (1) 3000; (2) 770; (3) 275; (4) 128; (5) 70; (6) 39.

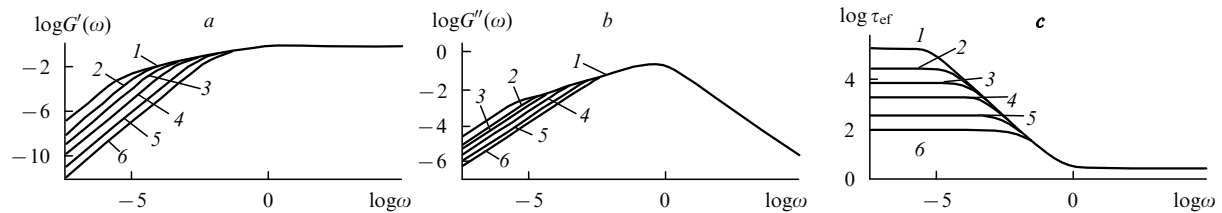


Figure 12. Frequency dependences of the real (a) and imaginary (b) parts of the elasticity modulus and of the effective relaxation time (c) in terms of the R-model equations. The chain length: (1) 501; (2) 201; (3) 101; (4) 51; (5) 21; (6) 11.

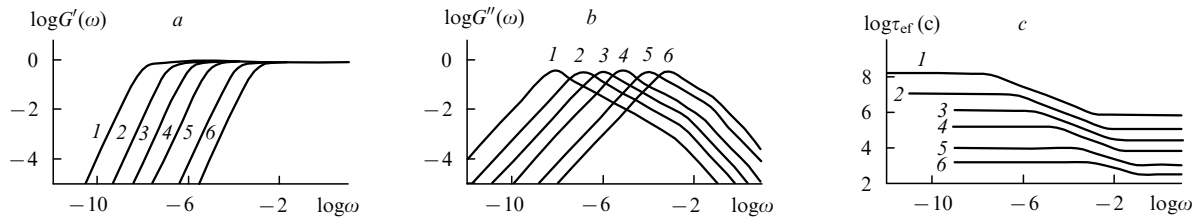


Figure 13. Frequency dependences of the real (a) and imaginary (b) parts of the elasticity modulus and of the effective relaxation time (c) in terms of the DE-model equations. The chain length: (1) 501; (2) 201; (3) 101; (4) 51; (5) 21; (6) 11.

R-model and to 1/2 for the DE-model, whereas according to experimental data, it makes up 0.2–0.3, the latter dependence being the more clear-cut the larger is the MM of polymers. The position of the maximum on the curves reflecting the frequency dependence of the imaginary part of the elasticity modulus depends on MM, though it is not cubic, as follows from the DE-model, but has the exponent 4, *i.e.*, it is analogous to the maximum relaxation time dependence.

Variation of the effective time of relaxation

$$\tau_{\text{ef}} = \frac{G'(\omega)}{\omega G''(\omega)} \quad (13)$$

also points to an appreciable distinction from the R- and DE-models, on the one hand, and to a discrepancy between the predictions based on these models and the experimental results, on the other: as in the case of the temporal dependence, on the curve reflecting the frequency dependence of the effective relaxation time one can differentiate two segments with constant values of minimal and maximal times and a transition region where τ_{ef} is proportional to the frequency (R-model) or to the square root of the frequency (DE-model). According to the experimental data, this dependence is expressed by the relation

$$\tau_{\text{ef}} \propto \omega^a,$$

where $0.5 < a < 1$.

Hence, the analysis of experimental data shows that the regularities of relaxation of such narrow fractions of linear polymers cannot be described even qualitatively by either the R-model or the DE-model.

The quantitative description of the relaxation of polymers based on the models considered faces serious difficulties; therefore, numerous semi-empirical and empirical approaches which recommend the use of exponential laws or dependences of the ‘stretched’ exponent type have appeared. For example, it is proposed^{125,132,133} to express the elasticity modulus relaxation with sums [see, *e.g.*, Eqns (9) and (11)] by analogy with the R-model, though with a different spectrum of relaxation times and a small number of the sum members. The physical meaning of such presentation is unclear.

There are equations of the type¹³⁴

$$G(t) \approx t^a e^{-\beta t},$$

which can be used for deriving the dependences of the elasticity modulus relaxation on the frequency of measurements of the type of the Havriliak–Negami dependence¹³⁵

$$G(\omega) \approx [1 + (\omega\tau)^2]^{-\alpha},$$

as well as the Kohlrausch–Williams–Watts equation

$$G(t) = a_1 \exp(-k_1 t^{\beta_1}) + a_2 \exp(-k_2 t^{\beta_2}).$$

Equations of this type often give a satisfactory description of the regularities of relaxation processes over a certain time or frequency interval. Attempts are being made to provide them with a theoretical base (*e.g.*, some studies^{122,136,137} were devoted to the development of coupling theory). It should however be noted that

no substantial progress concerning the region of highly elastic state has been achieved.

VII. Relaxation of chain orientation

The adequacy of a specific model is judged from the results of experimental studies on the orientation of non-cross-linked polymer chains in a concentrated solution, melt or a network polymer.^{10,13} According to current theoretical concepts, the orientation of chains in a non-cross-linked polymer is possible if the chain length exceeds the magnitude of M_e , *i.e.*, if in a given time interval the polymer chain is a network with its nodes formed by entanglements. However, many experimental studies^{138–145} have shown that oligomeric and short chains with the MM much lower than M_e can also be oriented in a polymeric matrix composed of the chains the MM of which is substantially larger than M_e or which form a network polymer. In this case, the motive force of the orientation is the so-called nematic interaction, *i.e.*, the manifestation of intermolecular forces of non-topological character.^{140,141} The nature of this interaction remains the subject of discussions (see, *e.g.*, Refs 142, 143). It was speculated that the important role is played by the free volume⁹ or configurational entropy in the implementation orientation.^{146–148}

It has been proposed^{142,143,149} that the coefficient ε determined by the relation

$$\langle \mathbf{u}_i \times \mathbf{u}_j \rangle_{\text{probe}} = \varepsilon \langle \mathbf{u}_i \times \mathbf{u}_j \rangle_{\text{matrix}}, \quad (14)$$

be used as the measure of nematic interaction where $\mathbf{u}_i$ and $\mathbf{u}_j$ are the components of the vector of orientation of monomeric chains.

The value of ε depends on the concentration and MM of short chains: as the concentration of long chains increases, the relaxation of the orientation of short chains is decelerated.¹⁴⁰ For example, the value of coefficient ε reaches 0.9 for short polybutadiene chains ($\text{MM} \leq 1000$) and decreases to 0.4 as the chain length increases (see Ref. 142). Approximately the same value of ε is characteristic of the nematic interaction in polybutadiene, ethylene–propylene^{140,150} and polystyrene¹⁵¹ block copolymers, as well as of the orientation of short molecules in the polydimethylstyrene¹⁵² and polyisoprene^{153,154} matrices. The value of ε equal to 1 was found for the polydimethylsiloxane matrix–oligomer system (see Refs 155, 156). Most studies have not revealed any temperature dependence of ε , though the opposite data are also available (see, *e.g.*, Refs 157–159).

Sotta¹⁶⁰ studied the phenomenon of a free segment orientation in a polymer network by the Monte Carlo method and found that $\varepsilon = 0.397$. The only factor whose action can explain the occurrence of orientation is the effect of excluded volume.

The theoretical approach to the estimation of ε magnitude developed by Merrill *et al.*¹⁶¹ consists in a modification of the DE-model and bears a semi-empirical character. This approach proposes the use of the notion of ‘nematic interaction’ of the end unit of a test chain with the matrix, though its physical meaning is not explained.

Upon introduction of groups capable of strong intermolecular interaction, *e.g.*, formation of hydrogen bonds, into polymeric chains, the coefficient ε increases substantially and becomes temperature-dependent.¹⁴⁹ This points to an important role

played in this phenomenon by the intermolecular interaction of energetic origin. However, an attempt at theoretical consideration of this factor¹⁶² did not go beyond the frame of empirical increment to the diffusion coefficient which takes into account the lifetime of the arising hydrogen bond.

It should be noted that the temperature dependence of the equilibrium constant of the reaction of hydrogen bond formation in macromolecular systems (polybutadienes with the MM ranging from 26 000 to 48 500) is markedly weaker than that in low-molecular systems (squalene):¹⁶³ as the temperature is increased from 20 to 100 °C, the equilibrium constant is changed 4-fold in the polymer and more than 10-fold in squalene. In contrast with the low-molecular model, the entropy of hydrogen bond formation decreases with temperature (provided the enthalpy remains constant, 28.6 kJ mol⁻¹). It may be presumed that weak intermolecular bonds (of the van der Waals type) will exhibit a still weaker temperature dependence. The effect of groups capable of forming hydrogen bonds that have been specially introduced in the polymeric chains on the relaxation properties of polymers is significant:^{163–169} the region of high-elasticity plateau is widened by several orders of magnitude with regard to frequency, the maximum of the $G''(\omega)$ is shifted to the low-frequency region also by a few orders; in addition, a shoulder appears on the low-frequency branch.^{163, 164, 167} Such changes occur upon addition of as little as 1%–4% of phenylurazole groups modifying polybutadiene. The observed effect of hydrogen bonds proves to be significantly stronger than the repetitive deceleration of the relaxation of polymeric chains.¹⁶⁵

VIII. The network of physical bonds as a dynamic factor

The effect of fluctuating physical entanglements on the dynamics of a macromolecule was studied by the Monte Carlo method¹⁷⁰ using a classical chain model on the Verdier–Stockmayer cubic lattice with two types of kinetic units.^{116, 117} The chain length was varied from 5 to 1000 monomeric units within the observation time intervals which made it possible to follow the motion of the chain as of an integral system. The behaviour of the chain was typical of the R-model, *i.e.*, the displacement of a random monomeric unit $g_m(t)$ obeyed the law expressed by relations (1).

If the chain was fixed on the lattice by a virtual network of physical bonds, the number of bonds and their lifetimes being set randomly, the dynamic behaviour of the chain had the features characteristic of the reptation diffusion, *i.e.*, at certain lifetimes and concentrations of nodes, at the distance equal to the medium-length chain scale a regime appeared determined by the relation (Fig. 14)

$$g_m(t) \propto t^\alpha,$$

where α was 0.25 (the value characteristic of the reptation regime) or even smaller. The motion of the chain mass-centre is characterised by the same dependence [see also relation (2)].

Consequently, the long-living fluctuating physical nodes can provide a polymer system with dynamic properties the manifestation of which is usually related to the availability of a network of topological nodes.

However, it is unclear whether the appearance of such type of fluctuating long-lived nodes in polymeric systems is possible above the glass transition temperature.

IX. On the nature of a physical network nodes

It is known that polymeric systems are characterised by rather strong intermolecular interactions of energetic origin above the glass transition temperature.¹ This is manifested, for instance, as the II-transition in their melts.¹⁷¹ This transition temperature is related to the glass transition temperature by the simple expression

$$T_{II} \approx (1.2 \pm 0.05)T_g.$$

In other words, supramolecular structural units are preserved up to the temperatures 20–60 °C higher than the glass transition temperature: in the opinion of Bershtein and Egorov,¹⁷¹ the liquid–liquid transition temperature T_{II} represents the upper temperature limit of the cooperative segmental motion.

Bartenev and Barteneva¹⁷² developed concepts of the λ -transition, *viz.*, the relaxation process characteristic of the highly elastic and liquid state of polymers. They argue that the λ -relaxation is determined by the existence, at temperatures above the glass transition temperature, of microvolume physical entanglements which have linear sizes ranging from 10 to 100 nm and

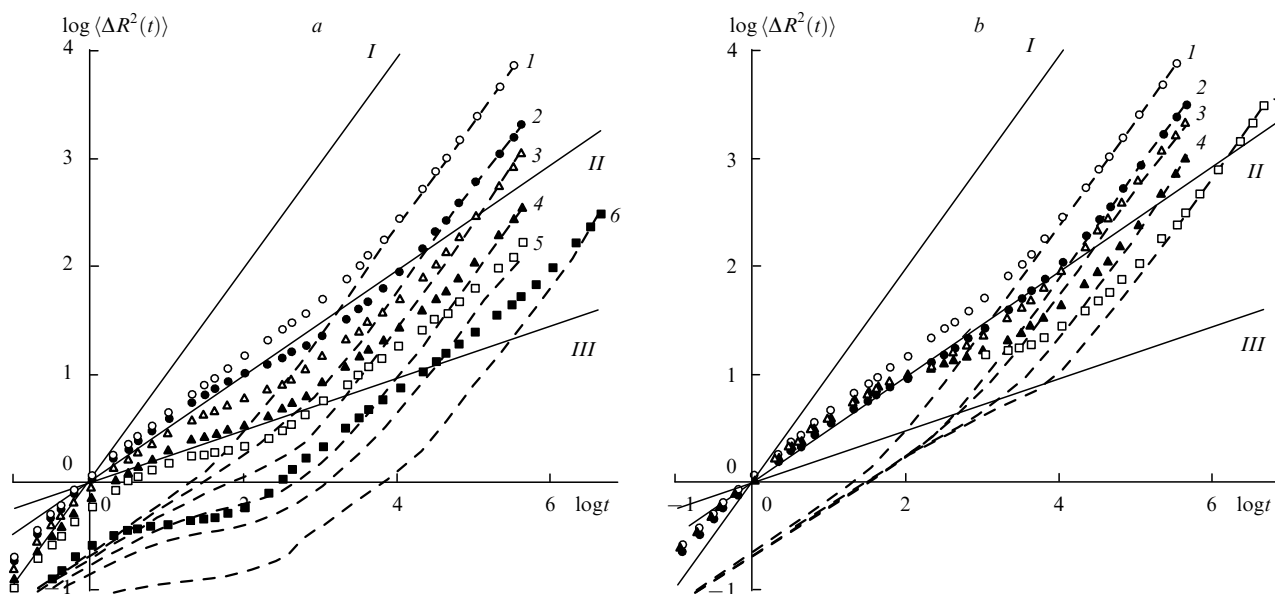


Figure 14. Dependence of displacements of a random monomeric unit and of the chain mass-centre (dashed lines) on time¹⁷⁰ for chains with the unit number $N = 100$ for different quantities of fixed monomeric units (p_f) with a lifetime (τ_f) of 6×10^3 (a) and 5% of fixed monomeric units (b) with different lifetimes; (a): $p_f = 0\%$ (I), 5% (2), 10% (3), 20% (4), 30% (5) and 60% (6); (b): $\tau_f = 0$ (I), 3×10^3 (2), 6×10^3 (3), 3×10^4 (4), 10^5 (5). For comparison, the Roman numerals I–III designate the lines with the slopes corresponding to t , $t^{1/2}$, $t^{1/4}$.

represent long-lived ($\sim 10^4 - 10^5$ s) fluctuations of the local orientation of segments.

Numerous data point to the formation of structural (including microphase) long-lived fluctuations. Thus the application of the techniques of static and dynamic light scattering has shown that¹⁷³ that large-scale density fluctuations occur in poly-(methyl-*p*-toluylsiloxane ($T_g = -17^\circ\text{C}$) up to 90°C . Poly-(methyl methacrylate) was found to preserve its ‘memory’ about the glass structure ($T_g = 65^\circ\text{C}$)¹⁷⁴ up to 132°C (^{13}C NMR). The use of EPR and NMR revealed¹⁷⁵ structural heterogeneities in a number of linear and network polyurethanes at temperatures $30 - 70^\circ\text{C}$ higher than the glass transition temperatures. The characteristic sizes of heterogeneities are ~ 10 nm, while their lifetimes are longer than 100 ms. The use of double-quantum NMR spectroscopy¹⁷⁶ revealed an anomalously high degree of orientation of monomeric units in the PB melt. It should be emphasised that the stability of heterogeneities (associates) is strongly dependent on the MM of polymers.^{176,177} Naturally, the trend towards the increase in the concentration of long-lived associates in polymeric systems is enhanced as the temperature is decreased and the solvent concentration is increased.¹⁷⁸

Simulation of properties of polymer solutions by the Monte Carlo method has shown¹⁷⁹ that there is a trend towards formation of dynamically fluctuating local domain structures with a parallel arrangement of segments if a polymeric chain is locally rigid. Mutual attraction of monomeric units enhances this effect.

Analogous results were obtained in a study of polymeric liquids of the *n*-alkane type by the method of molecular-dynamic simulation.¹⁸⁰ In this case, use was made of the Lennard–Jones potential with the energy of attractive interaction of non-bound monomeric units equal to 500 J mol^{-1} . The extent of ordering decreases with the increase in temperature, although its total collapse is observed at a temperature approximately twice as high as T_g .

Experimental studies^{181,182} indicate that associates of reactive oligomers substantially influence the kinetics of their polymerisation and the rate of relaxation processes in oligomer–polymer systems.¹⁸¹

We considered several clear examples of the existence of long-lived structures in polymeric melts, and numerous other examples can be found in recent reviews.^{1,182,183}

The role of intermolecular bonds in the manifestation of relaxation properties of polymers is great. It has been shown^{163,165} that even a small number of hydrogen bonds formed in a polymeric chain lead to an appreciable extension of the high-elasticity plateau. The presence of functional groups capable of association substantially influences the rheological properties of polymer systems.^{184,185}

A characteristic property of polymers is their ability to fix multicentre entanglements.^{186,187} Relevant computations¹⁸⁷ indicate that the lifetime of a complex formed by several bonds, with the energy of each bond reaching a value of the order of kT , increases exponentially as a function of the number of bonds, the exponent growing substantially as the energy increases (Fig. 15). In this case, the lifetime of the complex exceeds by many orders of magnitude the lifetime of a single bond. For example, the lifetime of a complex formed by three bonds ($10RT$) at 27°C is 1 s, whereas the lifetime of each bond is $\sim 10^{-9}$ s.¹⁸⁹ Such is the effect of connectivity! Even in the absence of energetically strong physical bonds, the monomeric units localised within the same volume element can remain in contact for a long time (which is at least twice as long as the time of release from the ‘tube’).^{32,190} In this situation, the number of such ‘contacting’ units is fairly large: it can amount to a half of the total number of units.¹⁹⁰ These results were obtained by the methods of molecular dynamics applied to systems in which only the impermeability of chains and the effect of excluded volume were taken into consideration. Ben-Naim *et al.*¹⁹⁰ believe that such long-lived contacts are formed due to the presence of entanglements, *viz.*, topological

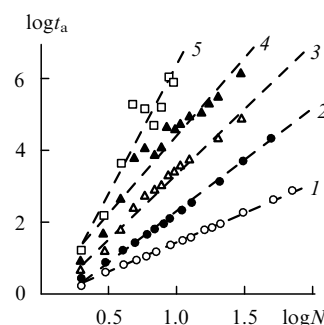


Figure 15. Dependence of the lifetime of associates t_a on the chain length N at different values of the bond energy;¹⁸⁸ E/kT : (1) 0; (2) 0.5; (3) 1.0; (4) 1.5; (5) 2.0.

nodes. However, in our opinion, in this case the nature of the nodes is not significant: the presence of some long-lived nodes leads to the appearance of others in long chains, and it is their ensemble that determines the dynamics of chains in concentrated systems.

X. Theoretical approaches other than the reptation model

Most theoretical approaches proposed for the description of dynamic properties of polymeric systems take into consideration the existence of a network of topological nodes.^{10,13,17–20,117} For this reason, there is no need to discuss them here. Instead, let us dwell briefly upon some new ideas.

1. The coupling theory

A series of reports (see the bibliography in Ref. 137) discuss various aspects of the coupling theory, the fundamentals of which were formulated by Ngai and Plazek.¹⁹¹ A modification of the R-model is used for describing the dynamics of low-molecular polymeric systems with the MM of a test chain exceeding certain critical MM which corresponds to the chain length between entanglements. The relaxation times τ_p of all modes increase proportionally to the magnitude $(t/t_c)^{n_p}$, where n_p is the coupling parameter, t_c is the time of transition of the test chain from the R-motion to a decelerated motion due to its interaction with the surrounding macromolecules. As a result, a simple exponent describing relaxation at short time intervals ($t < t_c$) is transformed into the ‘stretched’ exponent

$$\phi(t) = \exp \left[- \left(\frac{t}{\tau^*} \right)^{1-n} \right],$$

where τ^* is the effective relaxation time

$$\tau^* = \left(\frac{\tau_0}{t_c^n} \right)^{1/(1-n)}.$$

The latter relation takes into account the cooperative motion of the ‘test’ chain and the surrounding chains with a relaxation time characterising the motion of the non-interacting chain (τ_0).

The coupling parameter n varies from 0 to 1; it is dependent on the character of intermolecular interaction, and in many cases $n = 0.4$.

The proposed approach made it possible to describe to a good approximation a broad spectrum of dynamic experiments (see, *e.g.*, Ref. 137).

To our mind, the coupling theory is of a semi-empirical character, though its authors argue that this theory is based on fundamental ideas of classical mechanics with a chaotic structure determined by the non-harmonic (non-linear) nature of the interaction between molecules.¹³⁷ The authors do not provide any clear-cut physical justification of the relations used and confine themselves solely to claiming that any cooperative process

(be it segmental motion or motion of a polymeric chain) is described by the 'stretched' exponent.

2. The model of lateral diffusion

Some studies^{192–196} consider diffusion of contacts of a given chain with surrounding chains instead of the diffusive motion of the chain along the 'tube'. Since the diffusion occurs over the chain contour, the friction coefficient determined by the presence of contacts is time-dependent. Taking into account this fact and also the lifetimes of contacts measured by Herman^{192, 193} the following expression for the relaxation modulus was proposed:

$$G(t) = G_N \left[\sum_{j=1,3,\dots} \frac{8}{\pi^2 j^2} \exp\left(-\frac{j^2 A t^{2/3}}{N^2}\right) \right]^2,$$

where A and N are constants.

This model describes well the dependence of self-diffusion coefficient on MM in melts of PE, PEO and PDMS.¹⁹⁵ A characteristic feature of the model is the isotropic character of the motion of macromolecules in space, despite the fact that the coefficients of lateral and longitudinal (along the chain) diffusion differ, though not as substantially as predicted by the reptation model, which prohibits the lateral displacement of the chain.

The physical meaning of the approach proposed consists in that the friction elements (beads) of the R-model interact with the medium in a more complex manner; in such interactions, the friction coefficient depends on time and the composition of the system (concentration and MM of the matrix).

3. The monomolecular model

A generalised linear form of the equation of macromolecule dynamics in the monomolecular approximation has been proposed (see the bibliography in Refs 197, 198)

$$m \frac{d^2 r_i^a}{dt^2} = \int_0^\infty \beta(s) (\dot{r}_i^a - v_{ij} r_j^a)_{t-s} ds - \int_0^\infty \varphi(s) (\dot{r}_i^a - \omega_{ij} r_j^a)_{t-s} ds - 2\mu T A_{\alpha\gamma} r_i^\gamma + \phi_i^a(t), \quad (15)$$

where m is the mass of a Brownian particle which is associated with a segment of the macromolecule; r_{ij}^a is the coordinate of the point in which the particle having the number i, j and belonging to the macromolecule 'a' is located; $\beta(s)$ and $\varphi(s)$ are the memory functions; v_{ij} and ω_{ij} are the symmetrised and antisymmetrised components of the velocity gradient; μ and A are the coefficient and the matrix characterising the equilibrium form of the macromolecular coil; $t-s$ is the time interval; T is temperature and ϕ is the random force.

This approach allowed consideration of various hypotheses relative to the form of the memory functions $\beta(s)$ and $\varphi(s)$ and comparison of computational and experimental results. In particular, in a simple case of the single relaxation time τ :

$$\beta(s) = 2\xi\delta(s) + \frac{\xi}{\tau} B e^{-s/\tau},$$

where ξ is the liquid viscosity and $\delta(s)$ is the delta-function. In this expression, the relaxation time of the environment proves to be the characteristic relaxation time of the macromolecular coil. The increase in the parameter B , which is the measure in the increase of the particle friction coefficient due to the fact that during slow motions the probe chain pulls the tail from the surrounding macromolecules, obeys the exponential law:¹⁹⁷

$$B \propto M^b,$$

where $b > 2$.

The first term in the right hand part of Eqn (15) reflects the strength of the interchain interaction, while the second term expresses the strength of the internal resistance associated with changes in the macromolecular coil shape and determined by the

presence of surrounding molecules bound to the chain under consideration.

Equation (15) describes essentially the motion of an isolated macromolecule in a continuous medium possessing viscoelastic properties. Thus, the approach proposed takes into consideration the effect of the environment, *i.e.*, the theory does not go beyond the semi-empirical framework.

4. The mode-coupling theory

Over the last decade, following the publication of Schweizer's paper,¹⁹⁹ many studies have been reported which develop the model of local interaction of monomeric units of polymeric chains.

The theory of polymer mode-coupling makes an attempt to describe the chain motion at the microlevel under the action of fluctuating intermolecular forces.²⁰⁰

Microscopic description of the dynamics of a single polymeric chain in a condensed medium is performed using a non-Markovian generalisation of the Langevin equation with consideration of the fluctuating force of the intermolecular interaction. The central point of this theory is the conclusion about the memory function, which takes into account the local four-particle (two particles belonging to the probe chain and two others, to the neighbouring chains) contact; in this case, the effect of excluded volume, *i.e.*, the repulsion energy, is regarded as essential. The cell (contact) in which the above-mentioned interaction occurs behaves as an entanglement. These long-lived contacts are presumed to be distributed along the probe chain and their concentration to be proportional to the square root of the chain length (see the theory of local diffusion). It is also assumed that the existence of these contacts ensures high cooperativity of the motion of all segments of the probe chain, contrary to what is predicted by the simple R-model.

Thus, according to the mode-coupling theory, the relaxation of a polymeric system results from the highly cooperative but isotropic motion of the probe chain and the surrounding chains. It is still unclear whether this picture is realistic or the provided averagings overestimate the 'cellular' effect.²⁰¹

Schweizer *et al.*^{202, 203} have thoroughly reviewed and generalised the theoretical studies and the results of their comparison with the experimental data. It was shown that the conclusions drawn from the theory of polymer mode-coupling and the reptation theory are qualitatively analogous. The mode-coupling theory makes it possible to reveal the sensitivity of diffusion constants to various factors, such as fluctuation of concentrations, degree of polymerisation, composition of a mixture, temperature, concentration of a solution and proximity to the interface.²⁰¹

A disadvantage of this theory consists in a definite arbitrariness of the choice of the memory function mode (*cf.* the monomolecular model). Furthermore, a detailed analysis has shown²⁰⁴ that the renormalised procedure does not result in the convergence of results and, consequently, is physically incorrect.

5. The physical network model: relaxation of stress

A new approach has been proposed recently for considering the extent and character of the intermolecular interaction in polymeric systems within the frame of the physical network model.¹³⁰

Sufficiently long chains of networks with both covalent nodes and entanglements, as well as suspended 'tails' were found to exhibit some features of the R-relaxation (see, *e.g.*, Refs 205–207). It is therefore natural to represent a macromolecule as if it contained k R-subchains of length m connected by physical nodes. In this case, relaxation may be described in the frame of the R-model taking into account that the relaxation of the rigidity of the 'springs' connecting the nodes follows the R-mechanism, whereas the nodes themselves are characterised by a friction coefficient, which is determined by the interchain interaction and hence depends on the concentration and MM of a polymer.

The initial system of differential equations which describes the relaxation of the R-chain is expressed as⁷¹

$$\eta \frac{dy_i}{dt} = G(2y_i - y_{i+1} - y_{i-1}), \quad (16)$$

where y_i is the coordinate of the i th bead and G is the elasticity modulus of the spring connecting the friction nodes.

Solution of this system provides an expression for the temporal dependence of the elasticity modulus relaxation [see Eqn (9)].

The physical network model assumes that G is time-dependent. Introduction of the time function φ into Eqn (16):

$$\varphi(t) = \int_0^t G(\xi) d\xi,$$

and its solution yield the equation analogous to that for the R-model, though the expression of time in it is more complex:

$$G(t) = \frac{1}{k} \sum_{p=1}^k \exp\left(-p^2 \varphi \frac{t}{\tau}\right),$$

where

$$\varphi(t) = gt + \frac{\psi}{m} \sum_{q=1}^m q^{-2} \left[1 - \exp\left(-q^2 \frac{t}{\psi}\right)\right], \quad (17)$$

g is the elasticity modulus of the R-springs, $\psi = \psi_0 m^2$ is the maximum time of R-subchain relaxation and ψ_0 is the minimum relaxation time.

Evidently, the total chain length is

$$n = mk,$$

where k is proportional to the chain length. According to the R-model, the relaxation time τ is proportional to the squared chain length and to the friction coefficient. But the latter parameter *per se* should depend on n . This dependence is rather complex and its determination is a separate problem, though it may be presumed that the second power is a fairly reasonable magnitude. Thus, in conformity with the experimental results, we derive the general dependence $\tau \propto n^4$.

The relaxation curves calculated from Eqn (17) are qualitatively similar to the experimental curves.¹³⁰ Thus changes in the relaxation of elasticity modulus in the region of high-elasticity plateau are rather significant, and the dependence $G(t) \propto t^{-a}$, where $a \simeq 0.25$, is observed to hold over a certain interval. The segment of the exponential dependence with the exponent $1/2$ is absent if the number of nodes k is not too large. At longer times, the exponential decay is determined by the relaxation time which is proportional to the chain length raised to the fourth power (more precisely, to k^4); extrapolation of the curve to the ordinate axis gives a segment whose magnitude is dependent on the total length of the chain and the number of physical nodes:

$$\ln G(0) = -\ln k - \frac{\psi_0 n}{\tau_0 k^5} b - \frac{g}{\tau_0 k^4} t,$$

where $b = \sum_{p=1}^m p^{-2} \approx 1.6$ for sufficiently large m ; at $m \rightarrow \infty$,

$$b = \pi^2/6 = 1.645.$$

A detailed analysis of experimental results (including studies of diffusion of macromolecules, rheology of solutions and melts, frequency dependence of relaxation modulus, *etc.*) with consideration of physical bonds is a matter for the future, but even now one can discern good prospects for this approach for studying the dynamics of polymeric systems. For example, Walkenhorst²⁰⁸ showed that the process of physical network rearrangement is responsible for the long-term relaxation.

The concept of the network of physical nodes was used by Soloviev *et al.*^{209–211} for the description of the relaxation properties of elastomers. In these studies, analysis of the deformation curves differentiated two types of processes differing in their relaxation times: fast diffusive displacements of ‘free’ segments

which are not involved in the formation of intermolecular nodes of the physical network and a slow diffusive process of rearrangement of the network itself. Using basic postulates of non-equilibrium thermodynamics and considering the destruction of physical nodes as a reversible chemical reaction, these authors derived a system of equations which describe viscoelastic properties of elastomers over a wide range of deformation rates. Investigation of the stretching of copolymers of acrylamide with nonyl acrylate at the rates ranging from 1 to 0.01 s^{−1} and in the temperature range 20–120 °C has demonstrated that experimental data correlate with theoretical predictions. The approach of Soloviev *et al.* represents, in its essence, the development of Bartenev’s idea¹⁷² about the occurrence of a fast (α -process) a slow (λ -process) stages of the relaxation of elastomers.

Wientjes *et al.*²¹² made an attempt to employ the physical network model for describing rheological properties of polymers.

XI. Conclusion

This review has analysed the available experimental data on the dynamics of polymers with consideration of the network of physical bonds. It has been found that these data are at variance with the reptation model and that this model is insufficient for understanding the relaxation behaviour of polymers. The authors of this theory agree that the classical variant of the reptation theory yields results which are inconsistent in many respects with the experimental data.¹³ The attempts to refine the reptation model through consideration of the ‘tube’ relaxation and the disappearance of restricting entanglements^{13, 18} have resulted in a certain enhancement of the dependence of maximum relaxation time and viscosity on MM. These and analogous amendments ‘facilitate’ the relaxation process and decrease the relaxation times compared to those given by the simple non-modified theory. At the same time, the review demonstrates that the theoretical relaxation times are underestimated compared to those obtained experimentally, whereas the reptative behaviour is characteristic of the chains with the MM substantially larger than M_e .

The existence of a network of physical bonds confirmed experimentally is indisputable. However, its role in determining a broad spectrum of dynamic phenomena has not yet been elucidated. Unfortunately, the physical network model has not been developed to the extent reached, *e.g.*, by the reptation model. The investigators have still to clarify whether the intermolecular interactions play a role in the formation of relaxation properties of polymeric systems or these interactions merely make some contribution to the network of entanglements.^{213, 214}

The existence of the network of physical bonds is taken into account explicitly or implicitly in the consideration of dynamic properties of polymers. It underlies many approaches: for instance, some aspects of the problem of physical nodes and their effect on relaxation processes in polymers were discussed by Bartenev and Barteneva.¹⁷² As a matter of fact, the theory of polymer mode coupling also uses the physical network model (the network nodes are assumed to be areas with high local packing). The results reported by Sotta¹⁶⁰ point to an important role played by the network: orientation of a ‘free’ segment is brought about under the action of the oriented matrix without introduction of some energetic factors due only to the excluded volume effect.

Apparently, the fact that the temperature position of the beginning of the high-elasticity plateau (T_g) corresponds not to MM but rather to M_e , which is much smaller in order of magnitude than the corresponding size of the kinetic segment,²¹⁵ should be interpreted from the same viewpoint. This may imply that an important, if not decisive, significance in the physical network formation belongs to the high-density fluctuations, which seem to play the role of nuclei of the glassy state²¹⁶ or of the regions of local order in terms of the cluster model of the structure of amorphous polymers.²¹⁷

Only the existence of long-lived nodes of the network, and not their nature, is important for the manifestation of ‘reptative’

properties; therefore, the physical network model may be used for describing dynamic properties of a large number of systems ranging from physical gels to polymers with intermolecular interactions of the dispersive type.

It should be mentioned in conclusion that about three decades ago a vivid discussion was underway on whether or not such a structural formation as topological entanglements exists in polymeric systems. The discussion was initiated by the appearance of the 'packet' model of the structure of polymers²¹⁸ which was the antithesis of the 'felt' structure of Flory.⁷⁷ This discussion resulted in the triumph of the idea of entanglements not only in the structural respect; it also laid the foundation for the subsequent models of the dynamics of macromolecules. Now, the time has come for a new discussion on whether the entanglements do play the role ascribed to them in the dynamics of polymers or this role is at least overestimated.

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The chemical and adsorption effects of foreign molecules on the properties of high-temperature superconductors

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Abstract. Data on the effect of adsorption and intercalation of foreign molecules on the properties of high-temperature superconducting materials and on the reciprocal effect of superconductivity on the electronic state of adsorbed molecules are considered. Particular attention is given to the analysis of experimental conditions and interpretation of the results obtained. An effect of adsorbed molecules on the electrophysical state and the critical parameters of superconductors is noted. Specific features of the interaction between the phases in the superconducting state and the external molecules are discussed. The bibliography includes 280 references.

I. Introduction

The discovery of oxide materials which become superconductors at the liquid nitrogen temperature^{1,2} has resulted in a rapid development of studies of their physicochemical properties. These studies showed that the high-temperature superconductivity (HTSC) is extremely sensitive to the effect of the environment.

An opinion exists that superconductors are thermodynamically unstable systems.³ On the other hand, it was shown in one of the first reviews on the thermodynamic properties and stability of yttrium-containing superconducting ceramics⁴ that, although the $\text{YBa}_2\text{Cu}_3\text{O}_7$ phase is somewhat unstable thermodynamically, it can exist almost infinitely in this state. As a result of interaction of oxide ceramics with foreign molecules, superconductivity can both disappear and appear. Both of these phenomena have been observed experimentally in a study of the effect of the external molecules on the properties of HTSC oxides. Systematic analysis of the effect of foreign molecules on HTSC materials can help to reveal new ways for reaching high superconducting transition temperatures.

From the applied viewpoint, an important task is to obtain HTSC materials with high critical superconductivity parameters,

viz., temperature (T_c), current (I_c) and current density (J_c). Research on both classical low-temperature superconductors and HTSC materials has shown that high critical currents can be obtained if the superconductor structure incorporates an optimum number of defects acting as pinning centres for the Abrikosov vortices. Systematic studies of processes for the controlled formation of defects in superconducting materials has led to the conclusion that the intercalation of various chemical admixtures produces additional pinning centres, and hence increases the critical current density.

Recently, great interest arose in new electronic sensors which contain layers of organic molecules or polymeric films deposited on the surfaces of semiconductors or metals.^{5–7} Such elements have a significant advantage over the usual inorganic solid-state sensors, *i.e.*, enhanced sensitivity and selectivity with respect to environment.^{8–10} A novel class of oxide materials, *viz.*, high-temperature superconductors that possess a combination of unique physical properties at relatively high temperatures, has also become the subject of intense studies aimed at their application in similar electronic elements. For instance, it was found that molecular dye layers deposited on a Josephson junction made of superconductors increase considerably the sensitivities and selectivities of light sensors with respect to visible light.^{11–13} This was the first documented example of the effect of the properties of an HTSC material on the electron state of adsorbed organic molecules.

In this review, we have analysed the reported data on the effect of adsorption and intercalation of molecules on the physicochemical properties of ceramic and film HTSC materials and on the effect of the superconducting state on the low-temperature adsorption, catalysis and the electronic state of the molecules adsorbed on the HTSC material surfaces. Intensive studies are now being carried out along these lines, hence our review cannot claim to be comprehensive. In some cases, the interpretation of certain experimental results can be debatable. Nevertheless, the possibility of the reciprocal influence of the superconducting state and the molecular processes on the surface of HTSC materials is an established fact, which however requires detailed studies.

II. Some specific features of the physicochemical properties of high-temperature superconductors

All high-temperature superconductors are copper-containing oxides of complex chemical composition. As a rule, each unit cell of an HTSC phase incorporates from four to six chemical elements.¹⁴

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The data from small angle neutron scattering indicate that polycrystalline HTSC materials contain rather branched systems of pores connected to the surfaces of samples.¹⁵ Hence, molecules from the environment can readily penetrate into the specimen and react with the superconducting phase. The specific surface of such specimens measured by the Brunauer–Emmett–Teller (BET) method on the basis of the low-temperature nitrogen adsorption is from 0.2 to 1.5 m² g⁻¹, which is rather high for compact ceramic materials. The thermodynamic instabilities of HTSC materials can manifest themselves in their smaller stabilities in comparison with those of simpler low-temperature superconductors, *viz.*, metals and alloys.

Obviously, the effect of foreign molecules on HTSC materials can be rather complex. In addition, the study of these effects and particularly their interpretation can be complicated considerably because the surface chemical composition of an HTSC material differs significantly from its bulk composition.

In order to classify possible mechanisms of the interaction between the HTSC materials and the external molecules, it is worthwhile to consider some characteristic features of the structure of these materials and the mechanism of the initiation of the superconducting state.

1. Specific features of the structure of high-temperature superconducting oxides

Such multi-component oxide systems as La–Ba(Sr)–Cu–O, Y–Ba–Cu–O, Bi–Sr–Ca–Cu–O with perovskite-like or defective perovskite-like structures (Fig. 1) represent typical HTSC materials.^{16,17}

Virtually all HTSC materials are characterised by the existence of copper–oxygen layers and chains. The first and most important factor enabling superconductivity to appear is the existence of at least two types of copper coordination in the structural cell of the material; this results from the ability of the lattice copper ions to exist in several oxidation states, namely Cu(I), Cu(II) and Cu(III). Overlapping of the 3*d* orbitals of copper with the 2*p* orbital of oxygen results in the formation of a valence band and strong delocalisation of the holes.¹⁸ In the structure of CuO₂ (the copper–oxygen layers), the holes migrate along the oxygen anions, which makes the 3*d*⁹L-type electron configuration much more probable than 3*d*¹⁰L (where L is the oxygen vacancy).¹⁹ This specific behaviour of copper ions (in particular, the possibility of existence in several different coordinations) is

closely related to a manifestation of the Jahn–Teller effect by these ions.

The second factor responsible for the superconductivity of oxide systems is the low spatial dimensionality of the electronic structure, which is nearly two-dimensional. The low effective dimensionality of the electronic structure of HTSC materials results from the presence of the copper–oxygen layers (see Fig. 1). It is in these layers that the electrons providing the superconductivity are localised. The low structural dimensionality of an HTSC material is directly proved by strong anisotropy of superconductivity: the critical current along the crystallographic axes *a* and *b* is by an order of magnitude higher than that along the *c* axis.^{20,21}

The low dimensionality of the electronic structure is not the only factor which enables the possibility of existence of the superconducting state. For example, it has been shown²² that the superconductivity of La₂CuO₄ is much more strongly affected by violation of the stoichiometry of this oxide with respect to oxygen than by structural changes. The non-stoichiometry effect becomes more pronounced as the La : Cu atomic ratio decreases. The excess of copper favours the formation of additional oxygen vacancies; this facilitates the incorporation of oxygen during synthesis, resulting in partial oxidation of Cu²⁺ into Cu³⁺. Unlike La_{2–x}Cu^{II}O₄, the La_{2–x}Cu^{II/III}O₄ compound is a superconductor.

In YBa₂Cu₃O_{7–x}, violation of stoichiometry occurs due to the filling of the oxygen rows at the O(4) position (see Fig. 1*b*).^{23–25} The superconducting orthorhombic structure of YBa₂Cu₃O_{7–x} exists at the oxygen index *x* ≤ 0.6. For *x* > 0.6, the unit cell of this oxide is characterised by a non-superconducting tetragonal structure. Figure 2 shows the dependence of the superconducting transition temperature on the oxygen index *x*.²⁴ One can see that the quantity of the excess (or mobile) oxygen affects substantially the ceramics superconductivity.

The role of oxygen in HTSC materials has been discussed in several publications (see, *e.g.*, Refs 23, 24, 26–28). In the orthorhombic phase of YBa₂Cu₃O_{7–x}, oxygen can occupy different crystallographic positions:²⁷ the O(2) and O(3) positions in the [CuO₂] plane and two positions, O(1) and O(4), in the Cu–O chains (see Fig. 1*b*). The oxygen states O^{2–}, O[–] and O₂^{2–}, which exist in dynamic equilibrium and affect the superconducting and chemical properties of the majority of HTSC materials, have been predicted theoretically and found experimentally.²⁸ The high oxygen mobility in the material bulk is provided by the oxygen

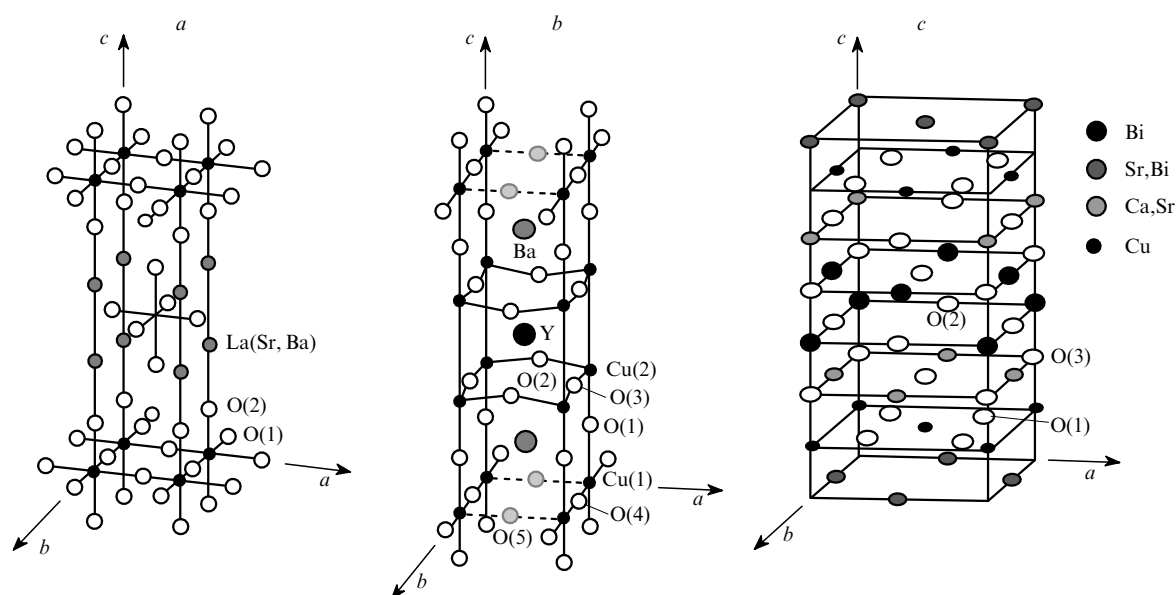


Figure 1. Unit cells of typical HTSC oxides.

(*a*), La_{2–x}Sr_x(Ba_x)CuO₄; (*b*), YBa₂Cu₃O_{7–x}; (*c*), Bi₂(Ca,Sr)₃Cu₂O_z (one half of the unit cell is shown).^{16,17}

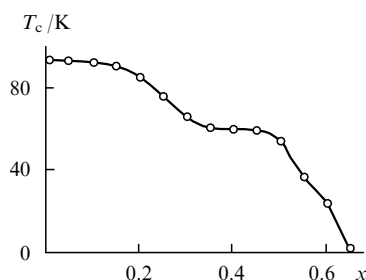


Figure 2. Dependence of T_c of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic on the oxygen index x .²⁴

forms which have the smallest charge or even no charge at all, whereas electron migration is provided by the O^{2-} ions.

2. Structures of polycrystalline specimens

Ceramic polycrystalline HTSC materials are of the greatest interest. This is due to their accessibility and relative simplicity of their preparation, which enables the synthesis of single-phase specimens with high superconducting transition temperatures. The main obstacles to the wide practical application of polycrystalline superconductors include the low critical currents and their rapid decrease as the field increases. In addition, ceramic HTSC materials have low corrosion resistance.

A polycrystalline HTSC material (ceramic) is a system of anisotropic superconducting granules with sizes ranging from 1 to 100 μm ; they are linked in a three-dimensional network of weak Josephson junctions.^{27,28} In a general case, a sandwich-like structure of the SNISN type appears on the boundaries between the granules (where S is a superconductor; N is a layer with normal metallic conductivity or a superconductor layer with a lower critical temperature; I is a dielectric or semiconductor layer). The thickness of the boundary layer allowing superconductivity current to flow between the granules should not exceed the coherence length along the crystallographic axis c [$\xi_c(0 \text{ K}) = 0.2 \text{ nm}$] and in the ab plane [$\xi_{ab}(0 \text{ K}) = 1.64 \text{ nm}$].²⁹

Weak bonds between the granules of ceramic HTSC materials differ in nature. In this review, we shall consider only those typical features of the structure and properties of inter-granule layers that can be affected by molecules foreign to the given material, namely: (1) non-stoichiometry of granules with respect to oxygen in the near-boundary layers; (2) high probability of admixture segregation at the inter-granule boundaries; (3) possibility of defective packing; (4) presence of 'foreign' or amorphous phases at the inter-granule boundaries.

The oxygen non-stoichiometry is due to surface rearrangement because of a decrease in the surface energy at the granule boundaries. The boundary layers with a high fraction of the lattice sites belonging to both contacting microcrystals are also energetically favourable.

Studies of admixture-free boundary granule layers of single-phase ceramic with composition $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (Refs 30–33) showed that enrichment of granules with copper and their depletion of oxygen occurs in a boundary layer no thicker than 5 nm. The phase formed at the granule boundaries has a orthorhombic structure.

Within the percolation theory based on the random distribution of oxygen defects, the critical oxygen deficiency (the oxygen index x) was determined; above this value, the oxygen-enriched structures (superconducting granules) are separated with insulating layers and the inter-granule superconductivity transport current is absent.³⁴ The value of x for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ HTSC ceramic found by the Monte Carlo method for a square lattice (two-dimensional superconductivity) was 0.26.³⁴

Segregation of admixture atoms and phases at granule boundaries seems to be the simplest and most natural reason for the formation of inter-granular layers possessing metallic conductiv-

ity and/or dielectric properties. In most cases, carbon and/or carbon-containing compounds constitute one of the main admixtures on the granule surfaces. Carbon can originate not only from the starting compounds used for the material synthesis, *e.g.*, barium carbonate, but also from atmospheric carbon dioxide.^{35–37} If excess BaCO_3 is present in the starting mixture for the ceramics synthesis, carbon is segregated on the granule boundaries and forms a coating 1–4 monolayers thick.³⁸ It is of note that carbon is not present on intergranule fractures.

In addition to carbon and its compounds, non-superconducting phases formed from the starting compounds due to incomplete synthesis were found on granule boundaries.^{39,40} For example, local melting at granule boundaries in copper–barium–yttrium HTSC materials at synthesis temperatures above 930 °C results in the formation of regions enriched with barium (the BaCuO_2 phase), yttrium (the BaY_2CuO_5 phase) or copper (the liquid phase).⁴¹

The formation of defective packing in the crystal structure at inter-granule boundaries and the formation of a twinning structure in the ceramic microcrystals are accompanied by relaxation of elastic stresses that appear upon structural phase transitions in the temperature range from 873 to 973 K. For example, the absolute majority of the granule boundaries of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramics contain inter-layers consisting of blocks of atomic planes CuO_2 – BaO – (CuO_2) – BaO_x *ca.* 1.5 nm thick; this is explained by the breaking of the layered structure in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. This process is similar to the formation of the $\text{YBa}_2\text{Cu}_4\text{O}_{7-x}$ phase with a critical temperature of 80 K.^{42–44} Since the coherence length along the axis c is 0.7 nm, the presence of such inter-layers on the boundaries of the majority of granules should have a strong adverse effect on the ability of the ceramics to conduct electric current.

The presence of the twinning structure inside the microcrystalline granules favours the formation of domains shaped as long (up to 1 nm) narrow 'bands' parallel to the (110) or ($\bar{1}\bar{1}0$) axes. The width of these domains varies from 5 to 300 nm and depends on the technique for the ceramic's synthesis and on the granule size.⁴⁵ These structures also deteriorate the current-carrying ability of HTSC materials.

3. Properties and structures of real high-temperature superconducting oxide surfaces

The interaction of the external molecules with an HTSC material starts at its surface. It has been noted above that, generally, the chemical composition, state, and structure at the surface and in the bulk of a superconductor differ considerably. However, the properties of the surface layer of an HTSC material affect directly the electronic properties and superconductivity parameters of the bulk phase.⁴⁶

The surfaces of the specimens are highly non-uniform. They contain macroscopic defects, such as growth steps, cracks, pores, dislocation exits, *etc.* Due to the interaction of coordination- and/or valence-unsaturated surface atoms with the external molecules, various chemical components are invariably present at the surface.

The adsorption of molecules and atoms often changes the properties of the surface itself, particularly the electron state of the surface atoms. The study of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic by photoemission spectroscopy revealed a difference in the state of the 'pure' and 'contaminated' surfaces.⁴⁷ Typical contaminations appear due to the chemisorption of the H_2O , CO, and CO_2 molecules. The content of surface carbonates on 'contaminated' specimens is 10 at.%–15 at.%, while that on a 'pure' specimen is 1 at.%. The surface also contains barium hydroxide, copper oxides, various yttrium compounds and the so-called 'green' phase, *i.e.*, Y_2BaCuO_5 . The surface copper exists in the Cu^+ and Cu^{2+} states;⁴⁸ the near-surface layer does not possess superconductivity.⁴⁹ It is therefore obvious that controlled surface cleaning is an important problem in studies on the effect of the surface states on the material superconductivity.

It is well known that chemical etching of polycrystalline films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with solutions of halogens and hydrogen halides in alcohols improves the stoichiometric composition of the surface and decreases considerably its contamination with carbonates and hydroxides.⁵⁰ For example, it was shown⁵¹ that the electric characteristics of the tunnel contact between the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film and metallic niobium are improved considerably after chemical etching of the film. In this case, an inter-layer of the SNS type is formed in which the surface resistance is almost 30 times smaller and the critical current is 40 times greater than those in contact *via* a non-cleaned surface. An inter-layer between the superconductors can be fabricated by chemical etching. Probably, this type of treatment of superconducting ceramics not only decreases considerably the surface contamination but also brings about certain chemical modification of the surface layer of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ system due to reactions of halogens and hydrogen halides with metal oxides on the surface. In fact, treatment of an $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film surface with a 1%–2% solution of Br_2 or HBr in ethanol results in the following surface compounds: YBr_3 , BaBr_2 and CuBr .⁵² Scanning electron microscopy did not reveal any significant changes in the surface morphology after chemical etching. It is important that surface treatment of this type increases its resistance against atmospheric gases.

Interesting results were obtained by bombardment of HTSC film surfaces with argon and oxygen ions. Bombardment with argon ions with an energy of 500 eV results in strong damage of the surface layer.^{23, 53} Oxygen atoms are preferentially removed from the surface and hence copper is reduced (while electroneutrality is maintained). This damage affects directly the oxygen vacancies and causes disordering of the near-surface layer atoms. As a result, the superconductivity characteristics of the films become much worse. However, the original properties of the films are completely restored after annealing in pure oxygen.

Quite a different picture is observed if the surface of an HTSC material is bombarded with oxygen ions.⁵⁴ In this case the surface etching rate is higher than that in the case of argon bombardment. After a brief bombardment, the dependence of the superconducting transition temperature for the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film on the etching time passes through a maximum with $\Delta T = 2$ K and then tends to the original value.

Hence, cleansing of the surface of an HTSC material by bombardment with oxygen ions is preferable to cleansing with argon ions. The mechanism of the effect of high-energy oxygen ions on the superconductivity transition temperature is not quite clear yet. However, it can be assumed that during bombardment with O^- ions, the surface layer, which is originally depleted of oxygen, is forcibly saturated with it, which favours the formation of the superconducting phase.

Although scribing (mechanical surface cleaning) of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic decreases the contamination with foreign molecules, it damages the surface considerably.⁵⁵ Studies of the surface by characteristic electron energy loss reflection spectroscopy showed that the near-surface layer contains an excess of barium and oxygen atoms, while the surface concentration of the copper–oxygen planes is insignificant. This is explained by the fact that scribing mostly results in microcrystal breaking along the inter-granule boundaries or at the Ba–O planes. In addition, preferential diffusion of the Ba–O complexes over the surface occurs.

One should pay attention to the nature and structure of the adsorption-active sites capable of adsorbing foreign molecules on the surfaces of HTSC materials. As shown in earlier studies,⁵⁶ the structures of real surfaces of oxide semiconductors and dielectrics are rather complex. The nature of the adsorption-active sites is determined by the state of oxygen in the near-surface region: deficiency or excess of oxygen give rise to electron-donating or electron-withdrawing active sites, respectively.

Studies of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic surface revealed active sites consisting of Cu^+ cations and an oxygen vacancy ($\square$, hole), which is an electron acceptor.⁵⁷ At room temperature, an active

site of the $[\text{Cu}^+, \square]$ type is stabilised by the elastic strain field of dislocations or by boundaries of twinning structures.⁵⁸ At 400 K, diffusion of the interstitial O^- ions begins to the sinks on the surface (holes or dislocation exits). Trapping of the O^- ion by the oxygen vacancy results in electrically neutral oxygen and a free electron. A fraction of the O^- ions reaching the Cu^{2+} surface ions can transfer a hole to them; this probably results in Cu^{3+} . Subsequent evolution of the active site at 580 K involves migration of neutral oxygen from the bulk; it ‘catalyses’ the decay of the $[\text{2Cu}^{3+}, \text{2O}^{2-}]$ site accompanied by the emission of the O^{2-} and Cu^{2+} ions to the surface.⁵⁹ The disappearance of the O_2^- bipolarons (local hole pairs) after the first heating *in vacuo* at 623 K makes the transition of this ceramic to the superconducting state at $T > 77.4$ K impossible.

The evolution of the state of oxygen on the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ surface at low temperatures was studied⁵⁹ by recording the transformation of the $\text{O}(1s)$ X-ray photoemission spectrum upon temperature decrease from 300 to 110 K. At 110 K, the O^- ions in the near-surface region are dimerised to give the O_2^- dimer, but the oxidation state of the copper ions remains unchanged. Simultaneously, the surface electric conductivity increases.

III. The effects of adsorption and intercalation of simple compounds on the properties of high-temperature superconductors

Intercalation of simple molecules into HTSC ceramics is accompanied by various physicochemical transformations: replacement of nodal atoms in the crystal lattice, intrusion of foreign molecules into the interstitial space, diffusion of molecules along the ceramic granule boundaries and formation of strong chemical bonds at the surface.

Unfortunately, the available experimental data do not allow yet an unambiguous conclusion regarding the nature of the interaction between small molecules and the superconductor material to be made.

For example, it is believed that the low-temperature adsorption of molecules on oxides is generally of physical character, hence it is non-specific and its dependence on the availability of adsorption sites and the electron state of the surface is insignificant. Physical adsorption can result in only small changes in the surface charge and the vibration modes of the surface atoms. However, in reality the adsorption of certain molecules on HTSC materials at $T < 300$ K affects their superconductivity; this cannot be explained by simple physical adsorption. As a rule, the changes in the superconductivity characteristics observed in these cases are related to intercalation or inclusion phenomena of molecules into the structure. The possibility of intercalation and chemical interaction of simple gases with HTSC materials at high temperatures (> 473 K) has been established reliably and does not raise doubts (see below).

1. The effect of oxygen

Oxygen plays a particularly important role in the formation of the structure of perovskite-like complex oxide materials and in their transition to the superconducting state. In addition, the oxygen molecule is a paramagnetic species, its adsorption on a superconductor surface can affect directly the superconducting properties. The techniques for obtaining HTSC materials and the role of oxygen in the formation of superconducting phases have been well covered in the literature. The reaction pathways of oxygen with HTSC materials during the synthesis and high-temperature treatment are so diverse that, despite a great number of publications, this phenomenon still remains insufficiently studied because the problem of non-stoichiometry with respect to oxygen and the related phenomena for the $\text{RBa}_3\text{Cu}_3\text{O}_z + \text{O}_2$ systems (where R is a rare-earth element) are excessively complex.⁶⁰ We shall only discuss the main aspects of such interactions.

One of the first Russian reviews devoted to the role of oxygen in HTSC materials was published in 1989.⁶¹ In the final stage of the synthesis, the oxide $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is saturated with oxygen. When compact ceramics are being obtained, this process is rather complicated, particularly in the synthesis of highly oxidised specimens ($x \rightarrow 0$). It was shown in a study of the oxidation kinetics of ceramic specimens of various densities at 773 K that slow oxygen absorption by compact ceramics results from transition of the reaction from the diffusion mode to the kinetic mode due to accumulation of considerable elastic strain in the material.⁶² Thermodynamic estimates showed that the elastic strain energy upon oxygen absorption by compact ceramics can affect the oxidation kinetics only in the case where the base planes contain oxygen ions of two types, namely, those strongly and weakly bound to the lattice.

The diffusion of oxygen into the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic was described⁶³ within a one-dimensional diffusion model. The equations obtained provide a good description of the experimental results on the oxygen exchange kinetics. The transformation of the specimens during oxygen diffusion in the temperature range of 423–973 K and at oxygen pressures of 1.4–10.7 atm involves three stages. A solid solution of oxygen in the tetragonal phase $\text{YBa}_2\text{Cu}_3\text{O}_6$ is formed in the first stage.⁶⁴ In this case, the diffusion factor is described by an Arrhenius dependence with the activation energy of 0.14 eV, while the pre-exponential factor depends on the oxygen pressure. In the second stage, oxygen starts to diffuse along unordered CuO chains in the tetragonal phase. The diffusion factor is also described by an Arrhenius dependence, but the activation energy is 0.6 eV and the pre-exponential factor no longer depends on the oxygen pressure. In the third (final) stage where the tetragonal phase is transformed to the orthorhombic one the diffusion factor becomes smaller than that in the tetragonal phase and gradually decreases to zero as the transition to the ideal orthorhombic phase of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ occurs.

Subsequent systematic studies of oxygen desorption from the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic at high temperatures showed^{65,66} that this process probably occurs according to a different mechanism. The main features of this process will be described in more detail below; for now, let us note that the adsorption of molecular oxygen on the surface of an HTSC material occurs according to the dissociation mechanism, whereas desorption occurs according to the association mechanism. The oxygen atoms occupy the vacant positions, *i.e.*, $\text{O}(1)$ or $\text{O}(5)$, in the near-surface layer of the crystal lattice. The exchange and transport of oxygen during the adsorption–desorption processes on the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic probably involves oxygen vacancies according to the relay-race mechanism.

The kinetics of oxygen evolution from the $\text{YBa}_2\text{Cu}_3\text{O}_{6.92-x}$ ceramic with $x < 0.54$ was studied in the temperature range of 600–950 K using the thermo-programmed desorption method.⁶⁵ At $T < T_m$ (where T_m is the temperature corresponding to the desorption peak maximum), the desorption rate is described fairly well by a second-order kinetic equation which is formally consistent with associative desorption. Oxygen-deficient specimens with $x < 0.25$ are characterised by a noticeable increase in the activation energy accompanied by an increase in the pre-exponential factor; this implies the presence of a compensation effect.

Many authors (see, *e.g.*, Refs 26, 67–69) consider the surface potential barrier as the main obstacle to the release of oxygen from HTSC materials. It was shown convincingly that the nature of this barrier is determined by the surface energy parameters.⁶⁹ For example, the oxygen desorption rate increased, whereas the desorption activation energy decreased by 0.2 ± 0.03 eV after vapour phase deposition of several monolayers of silver on the surface of a sample of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic. Changes in the surface properties should not affect the oxygen desorption rate if oxygen diffusion in the granules is the limiting step of this process. UV photoelectron spectroscopy data suggest that the electron work function for the yttrium ceramic's surface decreases by 0.3 eV upon vapour deposition of silver. It is thought that this

decreases the surface energy barrier.⁶⁹ The results of this experiment also indicate that the barrier is in fact energy-related rather than resulting from the formation of a particular surface structure. The temperature where oxygen starts to enter the ceramic was observed to decrease upon 'mild' treatment of the ceramic with molecular hydrogen.^{70,71} This is also evidence of the importance of surface barriers. The temperature of oxygen penetration into HTSC ceramics also decreased upon thermal vacuum treatment⁷² and after plasma treatment.⁷³

Several parameters characterising the surface potential barrier for the release of oxygen atoms were determined.⁷⁴ It was found by isotope exchange between the gas phase and the surface of a $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ single crystal under the conditions of isochronous and isothermal annealing of the specimens that the activation energy for oxygen desorption is 1.08 eV. In the authors' opinion, this indicates that the sorption mechanism of the formation of the surface barrier upon isotope exchange is somewhat preferable. However, an unambiguous conclusion on the surface barrier nature could not be made within the scope of this study. The use of polycrystalline specimens instead of single crystals does not affect the main results.

Degradation of HTSC materials at room temperature in the presence of water vapour is accompanied by the loss of oxygen from the HTSC phase. The water layer adsorbed on the superconductor surface probably favours the acceleration of oxygen exchange between the HTSC material and the gaseous environment.^{75,76} It was confirmed⁷⁵ that oxygen is desorbed at room temperature from the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic covered with an adsorbed water layer. In this case, the basic orthorhombic phase O_I is coated with a modified orthorhombic O_{II} phase with $T_c = 60$ K. The proportion of the O_{II} phase increases with an increase in the degree of hydration of the material and decreases upon annealing the specimen at 913 K.

The low-temperature oxygen exchange between the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic and the gas phase is limited by the surface potential barrier. Probably, the adsorbed layer of water molecules lowers this barrier significantly. On the other hand, it was shown theoretically⁷⁷ that the diffusion of O^{n-} oxygen ions inside the crystal lattice 'channels' $[1/2, b, 0]$, which can be regarded as the oxygen sublattice, occurs without activation and does not limit the redox processes. The hypothesis on the high mobility of oxygen in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ lattice at low temperatures was confirmed.⁷⁶ It should be noted that the high mobility can also involve a different mechanism. Based on thermogravimetric and X-ray diffraction analyses and electric conductivity measurements, a scheme for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ reduction at room temperature was suggested. According to this scheme, the oxygen diffusion is considered as an activationless process. Depending on the water vapour pressure, the stage limiting the oxygen exchange rate also changes. The oxygen exchange between $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and the gas phase at $p_{\text{H}_2\text{O}} \geq 760$ Pa is limited due to the presence of a chemisorbed water surface barrier. In the pressure range $250 < p_{\text{H}_2\text{O}} < 760$ Pa, the rate of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ reduction is limited by the step of O^{n-} anion diffusion through the layer of physically adsorbed H_2O molecules, while at $80 < p_{\text{H}_2\text{O}} < 250$ Pa, the movement of the O^{n-} anions is hindered by the twinning boundaries. At the lowest humidities ($p_{\text{H}_2\text{O}} < 80$ Pa), all the above factors no longer operate, and the reduction rate exceeds $0.15 \text{ mass } \% \text{ min}^{-1}$. However, a layer of the tetragonal phase is formed after some time on the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ surface; this layer does not conduct oxygen ions at low temperatures.

A study⁶⁶ of the oxygen isotope exchange between ^{18}O from the gas phase and ^{16}O from the $\text{YBa}_2\text{Cu}_3\text{O}_{6.92}$ ceramic in the temperature range of 293–923 K aimed at the elucidation of the nature of labile oxygen, which plays an important role in heterogeneous oxidation. The maximum oxygen isotope substitution at 923 K was 3.8 ± 0.3 a.u. per formula unit of the cuprate. It was assumed that the chain $[\text{O}(4)]$ and bridging $[\text{O}(1)]$ oxygen atoms in the cuprate crystal lattice are replaced almost completely. Hence, it is in these positions that labile oxygen, which probably partic-

ipates in catalytic oxidation on the surface of these ceramics at $T > 800$ K, is localised.

The inequality of the oxygen atom positions in the CuO_2 and ab planes results from the orthorhombic structure of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ crystal. According to the experimental data^{78–81} and theoretical calculations,⁸² the activation energies $E_a^{\text{O}(3)}$ and $E_a^{\text{O}(2)}$ for oxygen exchange between the O(3) and O(2) positions (see Fig. 1 b) are equal to 1.02 eV and 1.18 eV, respectively. The transition from the O(3) to the O(2) position occurs with an activation energy of

$$E_a^{\text{O}(3)} = E_0 - \Delta E,$$

and the transition from the O(2) to the O(3) position occurs with an activation energy of

$$E_a^{\text{O}(2)} = E_0 + \Delta E.$$

The difference between these energies, $2\Delta E = 0.16$ eV, is explained by the unequal O(3) and O(2) oxygen positions in the orthorhombic lattice, where the oxygen–copper bond along the a axis is longer than that along the b axis. To the first approximation, the ratio of the occupancies of these positions with oxygen is described by the Boltzmann equation

$$\frac{N_0^{\text{O}(3)}}{N_0^{\text{O}(2)}} = \exp\left(-\frac{2\Delta E}{kT}\right),$$

while the oxygen index is described by the expression

$$x = N_0^{\text{O}(3)} + N_0^{\text{O}(2)} - 1.$$

The features of oxygen ordering in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ($x \approx 0.1$) were studied by transmittance electron spectroscopy and electron microdiffraction.⁸³ Near the superconducting transition point, oxygen ordering occurs in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ crystal; this is accompanied by an increase in the orthorhombic parameter

$$R = \frac{|a - b|}{a + b}.$$

These results suggest that oxygen atoms can diffuse in the crystal even at liquid nitrogen temperature.

Based on elastic relaxation measurements in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic in the temperature range of 283–1073 K, the activation energy of oxygen exchange between the O(4) and O(5) positions (see Fig. 1 b)

$$E_a = 1.07 \text{ eV}$$

and the pre-exponential factor in the Arrhenius equation for the self-diffusion factor

$$D_0 = 1.8 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$$

were found for various oxygen partial pressures.⁷⁸ The activation energy decreases with an increase in the oxygen content in the ceramics. More detailed data on E_a and D_0 can be found elsewhere.⁶⁰

The phase stability of copper cuprates is directly related to the diffusion of labile oxygen. A novel technique based on direct coulometric titration was developed for the study of the redox kinetics of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and for the measurement of the oxygen diffusion factor under various conditions.⁸⁴ It was found experimentally that the oxygen diffusion factor in the specimens decreased monotonically with a decrease in x from 0.8 to 0.1. In the authors' opinion, this phenomenon can be explained by the vacancy-related oxygen diffusion mechanism. The temperature dependences of the measured diffusion factors obey the Arrhenius equation; these are in good agreement with previous results (see, e.g., the review²⁶). In continuation of these studies,⁸⁵ the phase stability limits of the compounds $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ ($R = \text{Y}, \text{Nd}$) were determined over a broad range of oxygen partial pressures. For $R = \text{Nd}$, the stability limit lies at higher temperatures than for $R = \text{Y}$. This is explained by a decrease in the energy of repulsion between the oxygen ions due to the larger distance between them

because of the larger ionic radius of Nd^{3+} . The dependences of the diffusion parameters (D_0 , E_a) on the oxygen non-stoichiometry index (x) and on the oxygen partial pressure were found. The diffusion of oxygen in the orthorhombic phase occurs faster than in the tetragonal phase. Practical recommendations were given for reducing the probability of microcrack formation, improving the contacts between the crystallites and shortening the low-temperature annealing when the HTSC ceramics are oxidised in the final stage of synthesis.

Studies on oxidation of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic under polythermal conditions showed that the temperature dependence of oxidation obeys the Arrhenius function, while the activation energy of this process changes monotonically as x increases.⁸⁶ In the ranges $0.2 < x < 0.3$ and $0.6 < x < 0.7$, the $E_a(x)$ dependence displays characteristic breaks. The authors suggest that this is closely related to a change in the mechanism of oxygen ion ordering in the CuO_2 planes. In the first case, a change in the oxidation mechanism results from the fact that 1/9 of the oxygen vacancies residing in the planar planes are occupied and their subsequent chaotic occupation is no longer possible. The second break most probably corresponds to the transformation of the tetragonal phase to the orthorhombic phase.

The diffusion of oxygen in $\text{Y}_{1-y}\text{Pr}_y\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ was studied⁸⁷ by measuring the electric conductivity of a sample in the temperature range of 300–1000 K. The desorption of oxygen from $\text{Y}_{1-y}\text{Pr}_y\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ was much slower than that from the pure $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase and decreased with an increase in y . The number of charge carriers in the ceramics studied was controlled by the oxygen content and did not depend on the Pr concentration.

The specific features of the thermal destruction of HTSC materials were analysed.⁸⁸ Analytical expressions for the dependence of the extent of oxygen non-stoichiometry on temperature and pressure were suggested on the basis of pseudo-chemical reaction models with consideration of the formation of point defects on copper ions and oxygen vacancies. It was found that the thermal destruction kinetics of high-temperature superconductors are described by chain nucleation equations.

A study of the processes of oxygen evolution from the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic upon thermal desorption *in vacuo* (10^{-5} Pa) revealed three characteristic temperature regions of oxygen evolution with maxima at 517, 673 and 932 K.⁸⁹ The first region corresponds to the loss of the chemisorbed, weakly bound oxygen; the second region, to the transformation of the ceramic from the orthorhombic phase to the tetragonal phase involving cleavage of the O–Cu(III) bonds; the third region, to the decomposition of this phase to give yttrium and barium cuprates as well as copper oxides with cleavage of the O–Cu(II) bonds. Thermogravimetric analysis of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic *in vacuo* at temperatures up to 1273 K revealed two temperature regions (673–873 and 1173–1233 K) where mass loss occurred due to the loss of oxygen.⁹⁰ The first region corresponds to the reversible oxygen loss related to a change in the copper oxidation state, $\text{Cu}^{2+} \rightarrow \text{Cu}^+$, whereas the second region corresponds to the irreversible oxygen loss accompanied by the destruction of the perovskite structure of the ceramics and formation of barium and yttrium cuprates.

Annealing of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic *in vacuo* at 10^{-3} Pa and 1073 K results in the destruction of the orthorhombic structure.⁹¹ On average, up to two oxygen atoms are removed from each unit cell, and the ceramic acquires a composition described by the formula $\text{YBa}_2\text{Cu}_3\text{O}_6$. Oxygen is completely removed from the O(4) positions (one atom per cell) and partially from other positions (see Fig. 1 b). The oxidation state of one-third of all copper ions becomes equal to unity. Annealing of the sample in air at 773 K results in the intercalation of oxygen into the material crystal structure; the overall number of oxygen atoms per unit cell reaches six.

The isothermal oxidation of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic comprises two stages, *viz.*, a diffusion-controlled stage and a 'slow' one

where the oxide is in equilibrium with the gas phase. The stepwise increase in the parameter x over time during the 'slow' stage was studied.^{92,93} This stepwise change in x is due to the structural transformation of the tetragonal phase to the orthorhombic one; as a result, mechanical stress is generated in the crystal, which is followed by its relaxation. This effect is described fairly well within the framework of a model which takes not only the T and p_{O_2} parameters but also the elastic intercrystallite interaction energy into account. The kinetics of oxidation of the $YBa_2Cu_3O_{7-x}$ ceramic in the temperature range of 748–873 K was explained⁹⁴ using a concept according to which the oxygen diffusion in the tetragonal cuprate phase occurs at the O(4) and O(5) vacancies and is thermally activated, while in the orthorhombic phase it occurs along specific structure 'channels' and does not require thermal activation. The oxygen migration in the orthorhombic phase is controlled by the interaction of the oxidant with the domain boundaries.

A study of the thermal stability of the orthorhombic phase of $YBa_2Cu_3O_{7-x}$ *in vacuo* and in oxygen showed that transformation of the orthorhombic phase to the tetragonal phase *in vacuo* (10^{-3} Pa) occurs at 973 K.⁹⁵ An increase in the oxygen pressure to 1 Pa increases the transformation temperature to 1073 K, while in pure oxygen, at a pressure of 10^5 Pa, this value is as high as 1173 K. A phase diagram that characterises the dependence of the temperature of transformation of the orthorhombic phase to the tetragonal phase on the oxygen pressure has been published.⁹⁶

Diffusion processes in thin superconducting films differ from those in bulk ceramic materials and single crystals. The diffusion of oxygen in thin epitaxial films of $GdBa_2Cu_3O_{7-x}$ was studied by measuring the electric resistance under isobaric and isothermal conditions in the temperature range of 650–1050 K.⁹⁷ Fast oxygen diffusion occurs preferentially at defects located along the c axis and with low activation energies. Chemical diffusion at vacancies occurs in the ab plane. The diffusion factor D in films thicker than 10 nm is $\sim 10^{-13}$ cm² s⁻¹. The thermal activation of diffusion is well described by an Arrhenius-type dependence and does not depend on the film thickness. At oxygen pressures around 10^2 Pa, the activation energy is 1.5 eV. However, if the film is thinner than 10 nm, the oxygen diffusion along the c axis is hindered due to the effect of the intermediate layer at the superconducting film–support interface.

It is important to establish the mechanism of the oxygen effect on the superconductivity parameters because it is necessary to solve the problem of the nature of the superconducting state.

Methods for the determination of the ΔH_{298}° , S_{298}° , and C_{p298} values and for the evaluation of the upper temperature threshold of superconducting transition of Y–Ba–Cu–O HTSC systems were developed with the use of thermodynamic simulation.⁹⁸ The oxygen content decreases abruptly in the temperature range of 200–500 K in complete agreement with the temperature dependences of Cu^{3+} concentration in the solutions studied. The Cu^{3+} concentration (at.%) as a function of the x index is described by linear equations for all solutions in the range of 100–900 K. For example, the equation for $YBa_2Cu_3O_z$ is

$$[Cu^{3+}] = -433.866 + 66.71538z, \quad (1)$$

where $z \geq 6.5$.

Direct comparison of the resulting Cu^{3+} concentrations with the z values for real superconductors is incorrect, since the structures of a superconductor and a model solution should be different, in accordance with the calculation conditions. However, the authors give certain recommendations regarding the applicability of the results obtained to the study of real superconductors. An equation was suggested for the superconducting Y–Ba–Cu–O system relating the Cu^{3+} concentration to the superconducting transition temperature (in K):

$$T_c = 45.32265 + 1.4333[Cu^{3+}]. \quad (2)$$

The inaccuracy of T_c calculation using Eqn (2) is considerable, since the phases obtained are usually thermodynamically unstable

under the conditions of synthesis. The correlation Eqns (1) and (2) can apparently be useful for rough estimates of T_c if the z index is known.

The application of the Langmuir–Maclin model made it possible to determine more accurately the oxygen diffusion factors in $YBa_2Cu_3O_{7-x}$ powdered superconducting ceramics at various temperatures.⁹⁹ The overestimated values for powders with particle sizes of 100 μ m were explained by the existence of 'easy pathways' for diffusion such as cracks, grain boundaries, etc., the role of which is particularly great for particles larger than separate superconductor crystallites.

A study of the physicochemical nature of oxygen dissolution and ordering of oxygen vacancies determining the superconducting properties of the $YBa_2Cu_3O_{7-x}$ ceramic¹⁰⁰ showed that an oxygen solution in the ceramic is somewhat comparable with an ideal gas (*i.e.*, obeys the Fermi–Dirac distribution), which is an important disagreement with the widespread concept of the 'regular' character of solid solution. The authors believe that the ordering of oxygen vacancies in the $YBa_2Cu_3O_{7-x}$ ceramic, which provides high-temperature superconductivity, results from structure transformations according to a mechanism related to the Jahn–Teller effect rather than from the interaction (repulsion) between the dissolved oxygen atoms.

The evolution of oxygen from the $YBa_2Cu_3O_{7-x}$, $La_{2-y}Ba_yCuO_x$, $Bi_4Ca_3Sr_3Cu_4O_x$, $Bi_{2-y}Pb_yCa_2Ba_2Cu_3O_x$ and $Tl_2Ca_2Ba_2Cu_3O_x$ ceramics *in vacuo* (10^{-4} Pa) with heating of the specimens to 1173 K was studied.¹⁰¹ At 773–923 K, oxygen evolution from the yttrium and thallium ceramics was observed. Oxygen was not evolved from the bismuth and lanthanum ceramics in the temperature range studied. According to the published data,⁸⁹ the evolution of oxygen from the $Bi_2Sr_2CaCu_2O_x$ system *in vacuo* occurs only in the temperature range of 1223–1323 K.

Thermogravimetric analysis showed¹⁰² that the $Bi_2Sr_2Ca_2Cu_4O_x$ ceramic contains over-stoichiometric oxygen: a specimen prepared in an oxygen atmosphere has the composition $Bi_2Sr_2Ca_2Cu_4O_{11.38}$. The existence of the excess oxygen is explained by the presence of copper ions in a high oxidation state (Cu^{3+}). This observation was also confirmed in other studies.^{103–105}

A considerable increase in the superconductor transition temperature of the $Bi_2Sr_2CaCu_2O_{8+x}$ ceramic was observed after it was annealed in oxygen.¹⁰⁶ Raman spectroscopy studies showed that oxygen is included in the Bi–O layers and the increase in T_c is due to the oxygen exchange between the Bi–O and Cu–O layers (see Fig. 1c).

The authors of the present review studied the effect of low-temperature (77.4–100 K) adsorption of O_2 , Ar and N_2 on the superconductivity of a $GdBa_2Cu_3O_{7-x}$ thin film.¹⁰⁷ All experiments were conducted *in situ* in an adsorption reactor placed in the probe of a magnetic susceptibility measuring device. The temperature dependence of the real and imaginary parts of magnetic susceptibility, $\chi'(T)$ and $\chi''(T)$, were recorded after the next gas portion was injected into the reactor at 77 K. All of the gases mentioned above affected the shape of the $\chi'(T)$ curve in the vicinity of T_c and 'shifted' the maximum of the $\chi''(T)$ curve towards the low-temperature region. The half-width of the $\chi''(T)$ peak decreased with an increase in the quantity of injected argon and nitrogen and increased upon injection of oxygen; this meant an increase and decrease in the critical currents in the superconducting film with an increase in the degree of its coverage with the gas molecules. The effects of the gases were reversible: removal of the adsorbed molecules by evacuation or by purging with helium at room temperature resulted in complete restoration of the original shapes of the $\chi'(T)$ and $\chi''(T)$ curves.

Comparison of experimental $\chi''(T)$ curves¹⁰⁷ with results of theoretical calculations for the hysteresis losses in thin superconductors^{108,109} afforded critical current densities extrapolated to 0 K, $J_c(0)$, and their dependence on the degree of surface coverage with adsorbed gas molecules (Fig. 3). The adsorption of

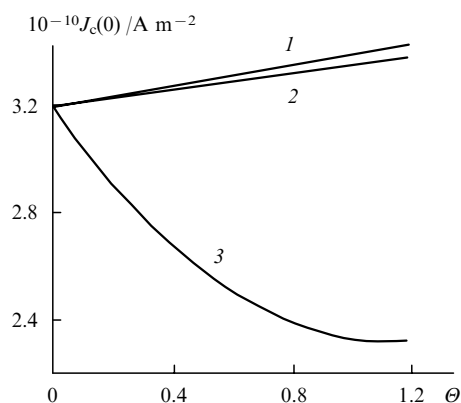


Figure 3. Dependence of J_c extrapolated to 0 K on the degree of coverage of the $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ film surface with N_2 (1), Ar (2) and O_2 (3) molecules.¹⁰⁷

argon and nitrogen is accompanied by a small increase in $J_c(0)$, whereas the adsorption of oxygen decreases this parameter. On the other hand, the superconducting transition temperature did not vary with an increase in the degree of surface coverage; only 'blurring' of this transition in the vicinity of T_c increased.

The decrease in the critical current density in the case of low-temperature oxygen adsorption is due to the effect of the paramagnetic O_2 molecule on the transport characteristics of the intergranular layers. In fact, the magnetic field strength at a distance from the adsorption site of an oxygen molecule equal to the diameter of this molecule is ~ 10 T. This field strength is quite sufficient for a total perturbation of superconductivity of the intergranular layers. The rather small decrease in the critical current density observed probably results from the fact that the distances of the adsorption sites of the oxygen molecules from the superconducting phase exceeds substantially the molecule size, *e.g.*, due to the presence of a 'buffer' non-superconducting oxide layer on the film surface.

The 'blurring' of the superconducting transition due to the low-temperature adsorption of oxygen, argon or nitrogen can be caused by many reasons. A most likely reason involves inclusion of the molecules of these gases directly into the crystal lattice of the material. This hypothesis was suggested long ago (see below) and was partially confirmed experimentally for argon adsorption.¹¹⁰ It is likely that the inclusion of simple molecules into polycrystalline HTSC oxides at low temperatures is facilitated by the presence of numerous defects and oxygen vacancies in the crystal lattices of these materials. For instance, the high surface defectiveness is indicated by experimental results of a study of electron photoemission from the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ surface¹¹¹ which showed that if the ceramic is crushed, the lattice oxygen leaves the surface instantly even at the liquid nitrogen temperature.

Similar changes in the superconductivity characteristics were recorded for the low-temperature adsorption of oxygen on the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic.¹¹² At 77.4 K, this adsorption results in a strong decrease in the transport critical current. The amplitude of the changes was much greater than that in the case of a superconducting film; this is probably due to the presence of a large number of weak bonds between the granules.

2. The effect of hydrogen

The specifics of the interaction of hydrogen with metal oxide superconductors primarily result from the presence of the O^{2-} and O^- ions and possibly O^0 in the anion sublattice; hydrogen readily forms chemical bonds with these species to give OH^- ions or water molecules.¹¹³ Hydrogen that has penetrated into the crystal lattice of an HTSC material reacts with the metal ions to change their effective oxidation state. All of these changes affect, directly or indirectly, the hole concentration in the CuO_2 plane, and hence, the superconducting transition temperature.

The neutron diffraction method was used to study hydrogen adsorption on the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic in the temperature range from 333 to 593 K.¹¹⁴ At low temperatures, hydrogen is preferentially adsorbed on the granule boundaries, but above 493 K, it undergoes chemical reactions with the superconductor material. Hydrogen adsorption at elevated temperatures results in partial amorphisation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ accompanied by the evolution of a considerable amount of metallic copper. According to the reported data,¹¹⁵ treatment of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic with hydrogen at 393–473 K results in a strong decrease in the low-field magnetic susceptibility and suppression of magnetic hysteresis at high fields. The superconducting transition temperature is not changed in this case. The suppression of the magnetic properties of the HTSC material is explained by the formation of metal hydrides in the inter-granular layers; the invariance of T_c is explained by the stable superconductivity of single crystals of the ceramic superconductor.

The $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic was treated with hydrogen at pressures of 1.3–10.0 kPa and temperatures of 393–483 K.^{116,117} This did not change the superconducting transition temperature. However, the formation of hydride and hydroxide phases [*e.g.*, CuH_2 , $\text{Ba}(\text{OH})_2$ and others] on the granule surfaces resulted in a decrease in the fraction of the superconducting phase, modification of the Josephson contacts, an increase in their electric conductivity and a decrease in the percolation conductivity.

It was found for the first time that the dependence of the critical current I_c on the quantity of hydrogen absorbed by the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic is non-monotonic and passes through a maximum at low concentrations of the latter.¹¹⁸ The position of the maximum depends on the specimen density and correlates with the minimum position on the electric resistance curve. Based on these data, the conclusion was made that the enhanced conductivity of the inter-granular layers at low concentrations of absorbed hydrogen is due to the reduction of oxides with hydrogen, which favours the formation of metallic copper and compaction of the layers between the granules, and due to additional ionic conductivity resulting from the presence of the H^+ and OH^- ions.

The superconductivity parameters of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic depend strongly on the oxygen concentration in the material lattice. It is well known that the oxygen-deficient $\text{YBa}_2\text{Cu}_3\text{O}_6$ ceramic is a semiconductor and displays antiferromagnetic properties, while the superoxidised $\text{YBa}_2\text{Cu}_3\text{O}_7$ ceramic has metallic properties. The effect of hydrogen inclusion into the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic with various oxygen contents at a temperature of 441 K in the pressure range from 1 to 3 atm was studied by the muon spin rotation method.¹¹⁹ It was shown that hydrogen intercalation results in magnetic ordering of the copper atoms; the amount of hydrogen required for this depends on the oxygen index: the more oxygen the ceramic contains the more hydrogen is required. Thus, hydrogen intercalation results in a formal decrease in the oxygen index. This requires one hydrogen atom per two oxygen atoms. It was concluded that hydrogen in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ plays the role of an electron donor which decreases the number of holes.

The intercalation of hydrogen into the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_2\text{Ca}_2\text{SrCu}_2\text{O}_{8+x}$ ceramics at 473–503 K and at a pressure of 0.9 atm was studied.¹²⁰ The concentration of holes in the superconductors decreased in a ratio of one hole per one hydrogen atom upon hydrogen intercalation. In addition, the superconducting transition temperature depended strongly on the position occupied by hydrogen in the lattice. It was thus concluded that T_c is primarily determined by the mobility of holes in the CuO_2 planes. This was confirmed by an X-ray diffraction study of the $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic.¹²¹ It was shown that the penetration of hydrogen into the material crystal structure along the CuO_2 planes begins at relatively low temperatures, 393–423 K, and at pressures of 5–10 kPa. A strong decrease in the thermal expansion factor was observed, which is believed to result from changes in the electronic structure of the material and the metal–dielectric

transition due to a decrease in the concentration of the oxygen vacancies.

A more detailed analysis of the hydrogen effect on the structure of yttrium and bismuth ceramics was made.¹²² The inclusion of hydrogen results in structural changes in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ lattice depending on the oxygen index.^{123–125} Subsequent saturation of the ceramic with hydrogen results in the formation of amorphous hydride phases where hydrogen occupies interstitial positions. A solid solution of hydrogen in the ceramic, similar to metal–hydrogen solid solutions, can be formed.

According to NMR data,¹²⁶ the diffusion of hydrogen into the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic occurs on the oxygen vacancies in the Cu–O chains and along the *a* or *b* axes on the interstices in the Y planes. The activation energies of these processes are 0.29 and 0.25 eV, respectively. The diffusion of hydrogen ceases following exposure of the ceramic to hydrogen at room temperature for three to four months, and the hydrogen atoms form strong O–H bonds. It was found by ^1H NMR spectroscopy that hydrogen diffusion also occurs in hydrogenated $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic at $T < 200$ K.¹²⁷ At temperatures from 130 to 92 K, the hydrogen atoms are mostly localised at the O(4) and O(5) lattice points. The inelastic neutron scattering and diffraction methods afforded the vibration spectra of hydrogen atoms in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic treated with hydrogen at 373 K.¹²⁸ Only several percent of the absorbed hydrogen participated in the formation of a solid solution; the H atoms occupy the octahedral positions formed by four Y atoms and two Cu atoms at the Cu(2) positions (Fig. 4). The rest of the hydrogen atoms are involved in an amorphous non-superconducting phase.

The NMR and X-ray diffraction methods were used to study the absorption of hydrogen and deuterium with the $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_3\text{O}_6$ ceramics at 473 K.¹²⁹ The incorporation of the hydrogen isotopes into $\text{YBa}_2\text{Cu}_3\text{O}_7$ results in partial removal of the chain oxygen from the O(1) positions and formation of O–H

bonds. No new bonds are formed in the $\text{YBa}_2\text{Cu}_3\text{O}_6$ ceramic, and no changes in the lattice parameters with increase in the hydrogen content are observed.

Pre-treatment of an yttrium HTSC ceramic *in vacuo* followed by treatment with hydrogen at 400–600 K and 2.6 kPa caused a considerable decrease (by 150 K) in the temperature at which oxygen enters the tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase.¹³⁰ The specimen became a superconductor ($T_c = 80$ K) after such low-temperature intercalation of oxygen; the ‘width’ of transition into the superconducting state was 15 K. If treatment of the specimen with oxygen is carried out at the same temperatures immediately after evacuation, it does not become a superconductor. It was shown¹³¹ that the decrease in the temperature at which oxygen enters the ceramics is caused by the transformation of the tetragonal phase of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ into the orthorhombic phase upon hydrogen treatment. The lattice parameter *b* decreases in this case since the hydrogen atoms occupy the oxygen vacancies along the direction *b* in the plane formed by CuO chains. Nevertheless, superconductivity is absent down to 4.2 K on cooling of the ceramics treated only with hydrogen. This is explained¹³¹ by the small orthorhombic parameter *R* which is 10^{-3} for the hydrogenated ceramics, whereas it is above 3×10^{-3} for the superconducting yttrium ceramics.

Similar changes in the physicochemical properties were observed upon treatment of superconducting bismuth oxides. The fraction of the superconducting phase and the superconducting transition temperature were found to decrease upon reduction of a $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_z$ single crystal with hydrogen (a 10 : 90 H_2 : N_2 mixture) at 673 K.¹³² Analysis of the X-ray absorption spectra led to the conclusion that reduction with hydrogen decreases the formal oxidation state of copper and the number of holes in the CuO_2 planes; this is the reason for the decrease in T_c .

In a study of the effect of hydrogen treatment on the structure of the bismuth-containing HTSC ceramic, the specimens were kept for several hours in a stream of hydrogen at 573 K.¹³³ Measurements of the electric conductivity of the specimens showed that the ceramic loses superconductivity completely and becomes a semiconductor. Hydrogenation of the ceramic results in a decrease in the unit cell volume, as shown by X-ray diffraction analysis. It should be noted that, on the contrary, hydrogenation of the yttrium HTSC ceramic increases the unit cell volume.

Thus, the type of effect of hydrogen on the properties of an HTSC material depends strongly on the treatment mode and temperature. At relatively low temperatures (up to 473 K), hydrogen mostly reacts with the granule surfaces and forms amorphous hydride phases involving metal atoms of the ceramic. In some cases, insignificant intercalation of hydrogen into the crystal structure of the material is observed. This phenomenon is accompanied by degradation of the magnetic properties of the superconductor and a decrease in the transport current density. As a rule, the superconducting transition temperature changes only slightly.

As the temperature of hydrogen treatment is increased, the superconductivity of HTSC materials decreases abruptly, until it is lost completely. This results from the incorporation of hydrogen into the crystal structure of the material which changes the T_c and the formal oxidation state of copper and decreases the concentration of holes in the CuO_2 planes.

High reactivity of hydrogen in the 400–470 K range found in a series of studies^{134–136} gives reasons to assume that the protonic conductivity of hydrogen-containing barium–yttrium cuprates is rather high. However, the originally high metallic conductivity of cuprates of the $\text{LnBa}_2\text{Cu}_3\text{O}_7$ family (where Ln indicates yttrium or another rare-earth element) ‘masks’ strongly weaker ionic conductivity. Studies of hydrogenated cuprates of the general formula $\text{H}_y\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ showed¹³⁷ that their specific resistivities increase by almost six orders if the hydrogen index *y* increases from 0 to 2 and decrease by three orders upon oxidation of the ceramics with *y* = 2 if the *x* index changes from 0.1 to 0.8.

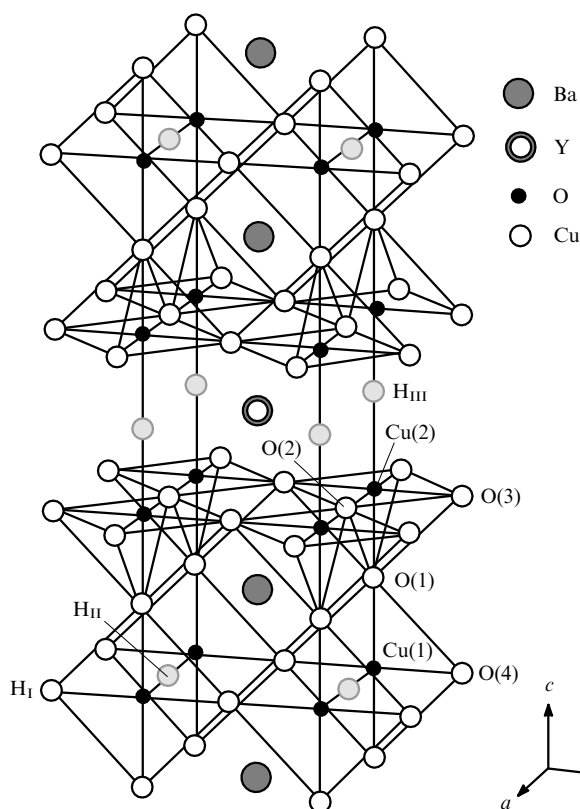


Figure 4. Possible locations of hydrogen atoms in the crystal lattice of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$.¹³⁸

Almost all aspects of the physicochemical interaction of hydrogen with superconducting cuprates were covered in one of the latest reviews on the effect of hydrogen on HTSC materials.¹³⁸ Figure 4 shows the crystal structure of the orthorhombic phase of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with indication of the positions where the hydrogen atoms are localised according to numerous studies. One can see that the intercalation of hydrogen atoms occurs along three main directions, *i.e.*, into the copper–oxygen bridges, chains and oxygen vacancies. However, the conductive CuO_2 layers remain unaffected. Hence, the observed changes in the electrophysical properties of HTSC materials are due to the electron density redistribution between the CuO_2 layers and the copper–oxygen chains $\text{O}-\text{Cu}(1)-\text{O}-\text{Cu}(1)-\text{O}$. As a rule, hydrogen intercalation into HTSC materials suppresses the superconductivity, while the superconducting transition temperature decreases (with rare exceptions). Figure 5 shows the dependence of the temperature of the onset of superconducting transition $T_{c,\text{on}}$ of an $\text{H}_y\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thin film on the hydrogen content. If the hydrogen concentration increases, $T_{c,\text{on}}$ decreases monotonically, while the transition width increases from 0.8 to 6.2 K. It should be noted that at the hydrogen content of ~ 0.3 atoms per cell, a sharp bend of the curve is observed; this correlates with the bend on the dependence of T_c on the oxygen content (see Fig. 2). This probably indicates that the hydrogen atoms (donors) react readily with weakly bound oxygen ions (electron acceptors), thus changing the concentration of the current carriers in the HTSC material.

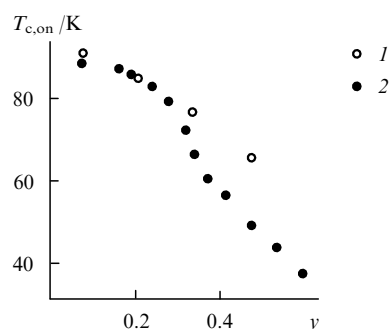


Figure 5. Dependence of the temperature of the onset of superconducting transition ($T_{c,\text{on}}$) of thin $\text{H}_y\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film on the hydrogen content (y) in unit cell;¹³⁸ (1) from electric resistance measurements; (2) from magnetic susceptibility measurements.

3. The effect of halogens

Numerous studies on the effect of the crystal structure and oxidation states of the chemical elements constituting an HTSC material on superconductivity showed that the holes serve as charge carriers in the superconducting state; these holes are genetically related to the p states of the oxygen ions, and their concentration is an important characteristic of a superconductor.^{139, 140} It thus follows that the anionic sublattice plays an essential role in superconductivity. One of the ways for changing the anionic sublattice defectivity involves doping with other anions, *e.g.*, halides.

The disappearance of electrical resistance at 155 K on $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ specimens synthesised with the use of BaF_2 as one of the starting reagents was detected for the first time in 1987 (Ref. 141). Since that publication, numerous studies on the replacement of the anionic sublattice by halogens have appeared. The presence of fluorine can both improve superconductivity^{142–149} and impair it.^{150, 151} For example, treatment of the $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ ceramic with $T_c = 65$ K with NF_3 at 613 K and with CCl_4 at 523–573 K increased T_c to 90 K in both cases.¹⁵² Presumably, the halogen atoms are incorporated in the O(4) position along the CuO chains, *i.e.*, in a sense, halogenation is similar to saturation of oxygen-deficient ceramics with oxygen. If

treatment is continued, the halogen anions occupy the O(5) positions but T_c is not increased any more. The effect of ‘soft’ fluorination on the degradation of powders of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ composition in a humid atmosphere was studied.¹⁵³ The fluorination of powders was carried out in 49% hydrofluoric acid vapour at room temperature in a closed vessel. The physical properties and superconductivity of the powders were almost unchanged, but their stability in humid atmosphere increased considerably. This phenomenon is rationalised as being due to the higher stability of the resulting fluorides, BaF_2 and CuF_2 , to water and prevention of further interaction of water with the superconductor granules. The presence of barium fluoride in synthesised thallium-containing ceramic cuprates with composition $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ doped with zirconium, hafnium, ruthenium and tin oxides improved their critical parameters noticeably.¹⁵⁴ However, there is no satisfactory explanation of the effect of barium fluoride on the properties of thallium-containing cuprates.

In a continuation of this work, the composition and properties of thallium-containing HTSC ceramics obtained in the presence of metal fluorides were studied.¹⁵⁵ The specimens modified in this way are characterised by higher content of the superconducting phase, smaller granule sizes and more pronounced transition in the superconducting state in comparison with the specimens obtained under the same conditions but without addition of fluorides.

Enrichment of the $(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_{1.6}\text{Ba}_{0.4}\text{Ca}_2\text{Cu}_3\text{O}_z$ ceramic with fluorine carried out by the addition of CuF_2 during the synthesis improves considerably its superconductivity.¹⁵⁶ The superconducting transition temperatures increase from 120 to 125 K, and the critical current density increases by 300%. According to X-ray diffraction data, the fluorine atoms replace the oxygen atoms in the CuO_2 plane. Changes in the morphology of the specimens due to the increase in the ceramic granule sizes are observed. The increase in T_c is explained¹⁵⁶ by optimisation of the concentration of charge carriers in the CuO_2 plane by the fluorine atoms, whereas in ceramics devoid of fluorine, the concentration of these carriers is apparently far from optimum because of the high oxygen content.

NMR and EPR spectroscopic methods were used to study the intercalation of halogens into the crystal lattice of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$.¹⁵⁷ The halogenation was carried out by exposing the specimens in a stream of gaseous NF_3 or CCl_4 diluted with N_2 at 573 and 523 K, respectively. The intercalated chlorine atoms are inserted in the chains between two copper atoms, while the fluorine atoms occupy the oxygen vacancies, as follows from the higher fluorine concentration in the materials with smaller oxygen indices.

The mechanism of the formation of halogen-containing HTSC phases based on $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ was studied.¹⁵⁸ The intercalation of halogens (Cl_2 , Br_2 , I_2) into the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ lattice was carried out in the temperature range of 423–523 K. An X-ray anomalous dispersion and Mössbauer spectroscopic studies of the specimens obtained showed that the interaction of halogens with the tetragonal phase of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ occurs as intercalation of halogens into the anionic vacant positions of the Cu(1) layer (see Fig. 1b). Charge transfer from the CuO_2 plane to halogens results in the formation of holes, which favours the manifestation of superconductivity ($60 < T_c < 93$ K) acquired by the resulting intercalation compounds. The chloride anion, unlike other halide anions, changes the ceramic’s microstructure owing to its large size; this results in the formation of stresses and dislocations and manifests itself as a decrease in the critical current. A study of the surface layers of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ tetragonal phase after its bombardment with chloride ions showed that implantation of chloride anions results in the formation of a orthorhombic phase layer near the surface; its thickness approximately equals the anion penetration depth.¹⁵⁹ This layer has the properties of a superconductor with a critical temperature of *ca.* 70 K.

In a study of chlorine-containing phases of the type $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{Cl}_y$ synthesised with the use of PCl_5 as a chlorinat-

ing agent, it was assumed¹⁶⁰ that at low temperatures the halogens are localised in chains around the copper atoms Cu(1) and the O(5) vacant positions are occupied first. An increase in the halogenation depth results in replacement of the O(4) chain oxygen atoms. Further halogenation under more drastic conditions results in replacement of the O(1) atoms, and the resulting phase has the limiting composition $\text{YBa}_2\text{Cu}_3\text{O}_4\text{Cl}_4$. The conclusion was made¹⁶⁰ that the decisive role in maintaining the superconductivity of halogen-containing phases belongs to the nature of the bridging atoms located at the O(1) position, which link the CuO_2 layers to the Cu(1) chain atoms: the electron-withdrawing properties of these bridging atoms induce superconductivity.

The change in the superconducting transition temperature due to the intercalation of HgBr_2 into polycrystalline $\text{Bi}_2\text{Sr}_{1.5-y}\text{La}_y\text{Ca}_{1.5}\text{Cu}_2\text{O}_x$ specimens with $0.0 \leq y \leq 0.4$ was studied.¹⁶¹ The specimens were obtained by keeping a tube containing certain weighed samples of HgBr_2 and the original superconducting ceramic at 508 K for 4 h *in vacuo*. An X-ray diffraction study showed that HgBr_2 is intercalated between the Bi—O planes. Figure 6 shows the dependence of T_c on y for the original and treated specimens. One can see that after treatment T_c decreases for the specimens with $y < 0.2$ and increases for the specimens with $y > 0.2$. It is believed that the intercalation of HgBr_2 changes the charge on the copper ions located in the conducting planes. The correlation relationships between the change in the copper charge (Δn) and T_c are reported;¹⁶¹ it follows from this relationship that Δn depends linearly on the concentration of the added compound and correlates with the concentration of the charge-carrying holes.

Upon treatment of non-superconducting ceramic specimens of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (tetragonal phase) with bromine vapour at 503 K and iodine vapour at 673 K without contact with air, they acquired superconductivity; the T_c values were 80–85 and 55 K, respectively.¹⁶²

The chemical interaction of iodine with the lattice copper ions can be a possible reason for the appearance of superconductivity in iodinated specimens. A similar assumption was made in a Raman spectroscopic study of the tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{6.1}$ ceramic treated in a iodine atmosphere. Iodine reacts with copper to 'extract' it from the lattice.¹⁶³ Oxygen is redistributed over the lattice, occupies the vacant sites in the chain and thus provides the possibility for superconductivity to occur. The same conclusion was also made in yet another study.¹⁶⁴ X-Ray diffraction analysis performed after annealing of the non-superconducting phase $\text{YBa}_2\text{Cu}_3\text{O}_6$ in iodine vapour at 553–653 K showed that the superconducting orthorhombic phase had appeared and reflexes of foreign phases were detected, which possibly corresponded to copper, barium and yttrium iodides. Treatment of the $\text{YBa}_2\text{Cu}_3\text{O}_7$ orthorhombic phase under similar conditions was not accompanied by either structural parameter changes or formation of

foreign phases. Annealing a powder mixture of the $\text{YBa}_2\text{Cu}_3\text{O}_6$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$ phases *in vacuo* at 493 K (which is much lower than the temperature of oxygen liberation, 623 K) was accompanied by the intergranular oxygen transfer from the $\text{YBa}_2\text{Cu}_3\text{O}_7$ phase to the $\text{YBa}_2\text{Cu}_3\text{O}_6$ phase and resulted in a phase with composition $\text{YBa}_2\text{Cu}_3\text{O}_{6.65}$. This suggests the high diffusion mobility of oxygen at low temperature in the lattices of the ceramics studied.

Thus, the basic mechanism of the effect of iodine on the superconducting properties of yttrium ceramics apparently involves oxygen transfer into the tetragonal phase; this oxygen can be liberated from the neighbouring phases under the effect of halogen atoms. Treatment of the tetragonal phase with iodine vapour at 543 K resulted in a continuous series of $\text{YBa}_2\text{Cu}_{3-y}\text{O}_x\text{I}_z$ solid solutions which possessed superconductivity.¹⁶⁵ The reaction of iodine with the crystal lattice of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ single crystals depends essentially on the initial oxygen content.¹⁶⁶ At the maximum oxygen content (the specimen with $T_c = 92$ K), no reaction of the crystals with iodine was observed. However, the stoichiometric cationic compositions of the crystals of orthorhombic ($T_c = 55$ –60 K) and tetragonal phases changed and an amorphous layer of varying thickness was formed on the surface; this was followed by complete destruction of the specimens. The penetration of iodine into the matrix was determined by the presence of oxygen vacancies in the principal planes. Ordering of the iodine atoms included in the crystal lattice was not observed.

Two-phase specimens were formed upon bromination: the original tetragonal phase coexisted with a orthorhombic phase in the ratio $\sim 1:1$. The iodinated specimens consisted completely of a orthorhombic phase. The parameters of the orthorhombic phases in the iodinated and brominated specimens are similar. Thus, the halogen atoms occupy presumably the vacancies of the O(4) type along the b axis (see Fig. 1b).¹⁶² It was assumed on the basis of EPR spectra that halogenation results in the transfer of negative charge to the CuO chains and formation of holes at the CuO_2 planes.

A study of iodine intercalation at 23 K into the $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-y}\text{Y}_y\text{Cu}_2\text{O}_8$ ceramic by X-ray diffraction analysis showed that iodine is incorporated in the BiO—OBi double layers in such a way that the distance between them increases.¹⁶⁷ The superconducting transition temperature decreases by 10 K because the concentration of the hole carriers exceeds the optimum level.

The effect of iodine and oxygen intercalation on the physical properties and superconductivity of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ single crystals was studied.¹⁶⁸ The starting single crystals and elementary iodine were sealed in an evacuated glass tube, heated to 453 K and kept for 330 h at the same temperature. The oxidation of single crystals with oxygen was carried out at 10 atm and 823 K for 140 h, or at 600 atm and 673 K for 320 h. The resistance and magnetic measurements of the thus treated samples showed that the dimensionality of the superconducting system changes from two to three, T_c decreases, and the activation energy of magnetic flux creep changes. According to the model suggested for the explanation of these phenomena, the HTSC material acquires a multilayered structure with alternation of the superconducting and normal layers due to the intercalation of iodine and oxygen. The 'proximity' effect results in the redistribution of the charge carriers between the layers and hence in changes in the physical properties and superconductivity parameters. The structural ordering of atoms in superconducting $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{I}_y\text{O}_x$ single crystals containing intercalated iodine was studied by low-energy electron diffraction, Auger and photoelectron spectroscopy on chipped surfaces, as well as by transmission electron spectroscopy.¹⁶⁹ It was shown that iodination results in a superstructure with ordered aggregates of iodine molecular complexes in the empty channels formed upon distortion of the original lattice by structural modulation.

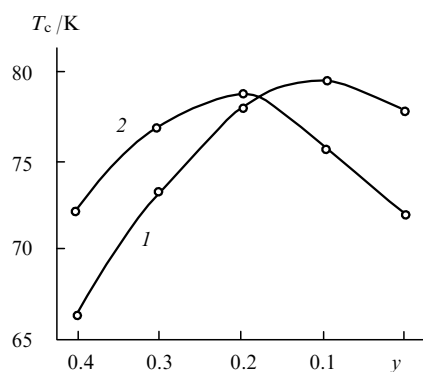


Figure 6. Dependence of the superconducting transition temperature of the $\text{Bi}_2\text{Sr}_{1.5-y}\text{La}_y\text{Ca}_{1.5}\text{Cu}_2\text{O}_x$ ceramic on y :¹⁶¹ (1) starting specimen; (2) sample after treatment with HgBr_2 .

In yet another study,¹⁷⁰ the intercalation of iodine in bismuth-based ceramics was carried out in a sealed tube, which was heated to 458 K over a period of 6 h and kept for 240 h at this temperature. According to the nuclear quadrupole resonance data, the iodinated $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ specimens contain no chemical bonds of the Bi–I and Cu–I types, *i.e.*, iodine in them is in atomic or molecular form and is truly intercalated. The superconducting transition temperature of the iodinated ceramic was 73 K.

Thus, halogenation of the yttrium-containing oxygen-deficient ceramic consisting of a $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ tetragonal phase results in orthorhombic phases with $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}\text{Hal}_y$ composition. The new phases have superconducting properties with approximately the same T_c as the usual superconducting ceramics, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. The iodinated ceramic is an exception, its T_c is no higher than the liquid nitrogen temperature. The formation of superconducting phases upon ceramics' halogenation is explained by inclusion of halogens at the oxygen O(1) positions; the halogens 'withdraw' the electronic charge from the CuO_2 planes onto themselves, which in turn increases the concentration of holes.

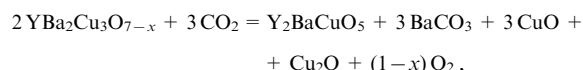
4. Degradation of high-temperature superconducting materials exposed to CO_2 and H_2O

Exposure of HTSC materials to atmospheric carbon dioxide and water results in their degradation accompanied by the loss of superconductivity and degradation of the superconducting phases. Therefore, the problem of storage and stabilisation of HTSC materials is of major importance. One of the first reviews on the chemical degradation of superconductors is found in Ref. 171.

The reaction of CO_2 with the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic starts at room temperature.¹⁷² The decrease in the critical intergranular current correlates with the intensity of the CO_2^+ peak in the mass spectra of the gases evolved from the ceramic; this suggests that carbonates are localised at the granule boundaries. When synthesis is carried out in the air at high temperatures, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ absorbs CO_2 . The maximum absorption is observed at 1173 K, and the amount of absorbed CO_2 with respect to carbon reaches 0.05% of the ceramic mass.¹⁷³ A study of the decomposition of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic in a 5% CO_2 + 95% O_2 mixture at 1088 K showed that the nuclei of the $\text{Y}_2\text{Cu}_2\text{O}_5$ and BaCO_3 phases are initially formed very fast, and then a 'green' phase of Y_2BaCuO_5 and CuO appears. The formation of BaCO_3 at the boundaries between the granules upon treatment of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with pure CO_2 at 1123 K for 2 h was reported.¹⁷⁴

The powdered $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic reacts with CO_2 at 1273 K both in the absence and in the presence of moisture to give decomposition products such as BaCO_3 , $\text{Y}_2\text{Cu}_2\text{O}_5$, CuO , Cu_2O and Y_2O_3 .¹⁷⁵ In the 90% CO_2 + 10% O_2 mixture, the decomposition products differ somewhat: they do not contain Cu_2O and Y_2O_3 .

A detailed study of the kinetics of the reaction between powdered $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and pure CO_2 in the temperature range of 823–1163 K was carried out.¹⁷⁶ The reaction of the ceramic with CO_2 can be described by the equation:



where Y_2BaCuO_5 is an intermediate. In the temperature range of 823–1088 K this reaction limits the overall rate of the process and has an order of 1.5 with respect to the ceramic; its activation energy is 95 kJ mol⁻¹. Subsequent 'carbonisation' of the ceramic occurs according to the equation:



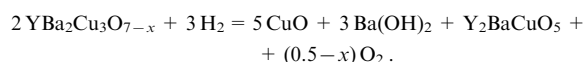
The presence of an alkaline-earth element in the HTSC ceramics provides a material with basic properties and hence makes it capable of absorbing CO_2 when in contact with air.

Calcination of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic during synthesis at 1223 K in air containing more than 1% carbon dioxide results in a non-superconducting tetragonal phase.¹⁷⁷ It is formed due to hindered oxygen exchange because of the formation of carbonate films on the material surface. The carbonates and decomposition products are mainly formed at the granule boundaries; this decreases considerably the critical intergranular current of the superconductor.

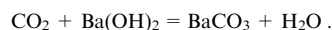
In the initial stage of the reaction of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with water vapour and carbon dioxide, the kinetics of water sorption is consistent with a process occurring at the internal grain boundaries and it is well described by a first order equation.¹⁷⁸ The diffusion of water vapour to the internal layers of the ceramic is the rate-determining step for CO_2 transfer. If the ceramic is pre-treated with water vapour, the CO_2 transfer occurs extremely quickly and is characterised by an effective diffusion factor exceeding 10⁻⁶ cm² s⁻¹. This is assumed to be due to water vapour condensation in the material pores.

Prolonged annealing of a $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_{1.7}\text{Ca}_{2.3}\text{Cu}_{3.0}\text{O}_{10+x}$ powder at 1123 K decreased slightly the carbon content in the specimen from 0.02 mass % after 24 h to 0.01 mass % after 192 h.¹⁷⁹ The powdered HTSC ceramic quickly absorbs carbon dioxide if stored in air: the content of carbon in the ceramic increases by a factor of two in 15 h, reaches 0.1 mass % in 240 h and then remains almost unchanged. An increase in the carbon content in bulk specimens from 0.019 mass % to 0.13 mass % is accompanied by a decrease in the critical current density from 280 to 150 A cm⁻².

The $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic readily reacts with water vapour even at room temperature to form the 'green' phase Y_2BaCuO_5 according to the equation:^{180, 181}



If this occurs in the presence of CO_2 , the resulting barium hydroxide immediately reacts with carbon dioxide:¹⁸²



Thus, in this case water acts as a catalyst of carbonate formation.

Owing to the high basicity of barium oxide, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ can react with CO_2 in humid atmospheres even at very small CO_2 partial pressures.¹⁸³ The products of hydration ageing of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic were studied.¹⁸⁴ The morphology of the new formations was studied using a scanning electron microscope. The original grain surface was rather smooth, but small protrusions and cracks appeared there after exposure to water vapour for one hour. If exposure was increased to 2.5 h, the ceramic's grains became covered with thin needles. An even longer exposure promoted the integration of the new formations which gradually covered the entire grain surfaces. X-Ray diffraction analysis showed that the new formations consist of barium hydroxide, $\alpha\text{-Ba(OH)}_2$, and the Y_2BaCuO_5 'green' phase.

Similar studies carried out using electromagnetic radiation absorption in the range of 1–3 MHz made it possible to follow the character of intergranular medium changes in specimens of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic exposed to moisture.¹⁸⁵ The changes in the chemical composition (degradation) of certain granules can occur at a depth of 0.3–1.0 μm from the surface depending on the specimen density. The formation of such a layer interferes with subsequent changes. Noticeable degradation of specimens with a density above 5.4 g cm⁻³ is observed in water after 10 h whereas in ordinary atmosphere it takes 5 months. Subsequent exposure to water little affects the superconductivity characteristics of the specimens.

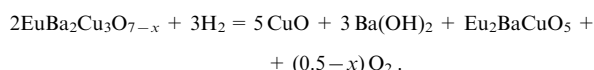
The surface state and microstructure affect the reaction of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic with water.¹⁸⁶ Generally, the average pore size in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic is $\sim 1 \mu\text{m}$ at an average grain size of 3–20 μm .¹⁸⁷ Analysis of data on small angle neutron scattering at the liquid nitrogen temperature led to the conclusion

that the majority of pores in the yttrium ceramic are open.¹⁸⁸ Thus, water can react not only with the outer but also with the inner surface by penetrating through the open pores. Water diffusion is an activation process. The activation energy is ~ 0.033 eV, this order of magnitude corresponding to the energy of a thermal quantum. Surface polishing of pellets of a sample accelerates the degradation three- to five-fold; apparently, this is caused by an increase in the number of open pores connected to the surface as a result of polishing. Hydration of textured specimens is strongly hindered, probably due to the small number of boundaries because of strong binding between the oriented grains, the concentration of oxygen vacancies in the intergranular spaces is rather small, and penetration of hydroxy groups inside the pellet is hindered. The penetration depth of water molecules into a textured specimen after ageing in water for 10 h at room temperature is 5 times smaller than the depth of its penetration into an isotropic ceramic.

Isothermal oxidation of hydrated $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic is accompanied by a stepwise increase in the sample mass, which indicates the presence of two oxidation steps, 'slow' and 'fast'.¹⁸⁹ The oxidation rate decreases proportionally to the water concentration in the material. The OH^- ions play a role of stoppers for defects of different dimensionality (oxygen ions, twinning structure boundaries) in their movement through the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ lattice. Presumably, during the 'slow' oxidation stage of the yttrium ceramic, the boundaries of the twinning structure between the crystallites of this compound are in the state of accelerated movement due to thermal activation and 'stripping' of these boundaries from localised proton-containing ions in the near-surface zone. Subsequent movement of these boundaries occurs in the matrix free of impurities.

The $\text{YBa}_2\text{Cu}_4\text{O}_8$ ceramic and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ specimens with an admixture of silver are much more stable against moisture than non-doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic.^{190, 191} This is explained by a more compact arrangement of granules consolidated by metallic silver particles in doped ceramics; this evidently interferes with fast diffusion of the water molecules in the material bulk. The effect of silver on the stability of powders with composition $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ in a humid atmosphere was studied.¹⁹² The composition of the surface was studied using an electron probe X-ray microanalyser and X-ray photoelectron spectroscopy. If the water content in the powder is above 1.6 mass %, silver (5 mass % – 15 mass %) has a stabilising effect. In order to increase the critical current, it is recommended to add 15 mass % of silver to the moist powder (1.6 mass % H_2O). On the surfaces of ceramics containing this amount of silver, the latter is present in the form of separate inclusions. At the Ag content of 5 mass % – 15 mass %, superconductivities of the ceramics remain practically the same as those for the original $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ specimen.

If the $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic is treated with water, the evolution of oxygen is preceded by dissolution of an insignificant amount of Ba^{2+} ions ($\sim 7\%$ of the total amount of barium in the ceramic).¹⁹³ The europium ceramic is much more stable than the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic, which undergoes 50% decomposition in a humid atmosphere at room temperature. Noticeable decomposition of $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$ (i.e. evolution of gaseous O_2 and passage of Ba^{2+} cations into solution) starts 2 h after the contact with water at 333 K and occurs according to the equation:



The decomposition of the ceramic at 353 K starts almost immediately. Complete reduction of Cu^{3+} to Cu^{2+} occurs only at 373 K. The decomposition of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic in distilled water and in solutions of sodium sulfate and barium chloride was studied.¹⁹⁴ It was shown that the presence of barium ions interferes with the hydrolytic decomposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$; after treatment with 10^{-2} M aqueous solution of BaCl_2 , the ceramic retains superconductivity even after boiling.

Hydrolysis of the ceramic is accompanied by leaching of barium cations, and addition of sulfate ions to water which binds barium ions causes complete decomposition of the superconductor. This is explained by equilibrium displacement upon changes in the reaction product concentration in accordance with the thermodynamic laws.

An interesting feature of the behaviour of water present in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic was noted.¹⁹⁵ It was found that the superconducting phase cannot release water at temperatures of oxidative annealing (673–873 K). It is believed that this results from geometrical factors related to lattice distortion as a result of oxidative annealing, which hinders the exit of proton-containing ions from the O(5) positions.

It was found by thermal desorption methods that water on the surface of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic can be physically adsorbed and structurally bound (in the latter case, the bond energy equals 145 kJ mol^{-1}).^{196, 197} The water molecules can occupy two types of positions, viz., the position in the yttrium plane between the CuO_2 planes and the position between two Cu(1) copper atoms (see Fig. 4).

EPR studies showed¹⁹⁸ that inclusion of water molecules into the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ lattice results in the appearance of the Cu^{2+} paramagnetic centres at the Cu(2) positions in the CuO_2 layers. The EPR signal intensity depends on the water content in the ceramic. It is assumed that these paramagnetic centres are formed due to non-uniform deformation along the CuO_2 plane rather than due to decomposition of the material.

A radiothermoluminescence study of the moisture-induced degradation of the $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$ type HTSC materials (R = Y, Sm, Eu, Ho) showed that barium hydroxide is the compound responsible for radiothermoluminescence.¹⁹⁹ The radiation intensity is much lower if the specimen contains a minor amount of the original compounds which did not react under the conditions of solid-phase synthesis of the HTSC material.

The possibility of protection of materials based on $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ from degradation in water vapour by applying coatings of paraffin, poly(vinylbutyral) and oxidised triglycerides of unsaturated fatty acids was studied.²⁰⁰ The last named was found to be the most effective.

5. The effect of Ar, He and N_2 adsorption

Noble gases, viz., Ar and He, as well as N_2 , do not react chemically with the material, and hence, the major factors of their effect on superconductivity can involve inclusion into the crystal structure of the material or surface 'charging' due to adsorption.

The effect of argon on the electric conductivity of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic was studied.¹¹⁰ The specimens were kept for several days *in vacuo* (10^{-3} Pa) at room temperature, then purged for three days with pure argon at the same temperature. After that, they were analysed by the resistance method at currents of 50, 500 and 5000 μA . An abnormal dependence of the electric conductivity on temperature was found when the latter was increased from 200 to 300 K: the resistance of a sample abruptly almost doubled at a current of 50 μA ; the increase was only several percent at 500 μA , whereas no abnormal increase in resistance at all was observed at 5000 μA . Apparently, this dependence of the electric resistance on current in this temperature range cannot be due to any manifestation of superconductivity. An increase in the current flowing through a superconducting specimen should result in the violation of the superconducting state and in the increase in resistance, rather than in the opposite effect observed in the experiment.

An Auger scanning microscopic study of specimens treated with argon revealed the presence of argon atoms in the near-surface layer ($\sim 100 \text{ \AA}$). The observed phenomenon is explained¹¹⁰ by the oxygen disordering in the lattice on the superconductor surface and the formation of a tetragonal non-superconducting phase, which is responsible for the resistance increase, in the gaps between the granules. However, the resistance of the specimens treated with argon decreased with a decrease in

temperature. Apparently, this is due to the fact that below room temperature, oxygen and oxygen vacancies can become ordered, and the semi-conducting tetragonal phase can be transformed to the orthorhombic phase, which displays metallic properties.²⁰¹

An increase in T_c and J_c due to intercalation of simple gases into HTSC ceramics was observed repeatedly.^{110, 202–204} However, no reliable information on this phenomenon is available so far. Apparently, this can be associated with a very strong dependence of superconductivity of a material on its structure; because of this, small and hardly controlled changes in the crystal lattice parameters due to intercalation can change essentially the properties affecting superconductivity.

A substantial increase in T_c was observed upon low-temperature (~ 78 K) treatment of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductor in N_2 , Ar, O_2 and He streams.²⁰³ In particular, T_c increased from 90 to 141 K upon treatment with nitrogen. Treatment with hydrogen did not affect T_c . The change in the superconducting transition temperature correlates with the duration of treatment. The change in the parameters of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductivity was assumed to be due to the inclusion of the gas molecules in the superconductor lattice. This changes the energetic state of the lattice and hence increases the energy of interaction between the carriers of superconductivity current, *i.e.*, the Cooper pairs. If the temperature increases, the gas starts to desorb; the Cooper pairs become unstable, and the superconductor passes in the normal (non-superconducting) state. However, it is unclear from this explanation why gases as different in nature as nitrogen, argon, oxygen and helium behave similarly. It is known, for example, that helium is not adsorbed at all on solid surfaces at the liquid nitrogen temperature.²⁰⁵

In an attempt to reproduce the effects described above, Granados *et al.*²⁰⁶ failed to observe an increase in T_c during low-temperature treatment of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic with helium. Therefore, the results considered above are attributed to experimental errors. A reason for the T_c increase could involve the rather fast heating of the specimen, which at certain helium pressures usually results in overestimation of T_c in resistance measurements.

Low-temperature treatment (77.4 K) of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic with nitrogen at normal pressure and with hydrogen at pressures up to 300 atm resulted in changes in T_c which increased or decreased depending on the duration of treatment.²⁰⁴ Similar results were obtained upon treatment of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with benzonitrile. After keeping the specimen in liquid benzonitrile for 11 h at room temperature, the T_c increased by 2 K. The T_c value was determined by measuring the electric resistance and magnetic susceptibility of a superconductor heated from 77.4 to 100 K. After several measurements, the original T_c value was almost restored. The similar effect of foreign molecules with completely different chemical properties on the superconductivity of the oxide $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ led to the conclusion²⁰⁴ that foreign molecules penetrate into the ceramics due to diffusion along the granule boundaries and microcracks, thus creating mechanical stress.^{207–209} The adsorbed phase propagating along the surface of a granule or a microcrack ‘bursts open’ the granules at the contact site, and the resulting mechanical stress can be quite strong. In the zones adjacent to the crack mouths, the ceramic material appears to be under huge pressure, which is believed to result in a local change in the superconducting transition temperature.

IV. The effects of adsorption and intercalation of organic molecules on the properties of high-temperature superconductors

The effects of organic compounds on the properties of superconductors are considerably more diverse than those of simple molecules. They can affect HTSC materials due to a number of their specific properties (ability to form complexes with metal

ions, to create regular layered structures that have electric conductivity, to be mechanically implanted in the superconductor material, to form charge transfer complexes), and also due to the possible presence of stable paramagnetic centres in their molecules.

1. Adsorption of organic compounds

The effects of adsorption of organic compounds on superconductivity was first studied on films of low-temperature metal superconductors.^{210–214} The adsorption of 3,4,7,8-tetramethyl-1,10-phenanthroline (TMP) on a thin vanadium film increased the superconducting transition temperature by 0.09 K.²¹⁰ The assumption was made that this effect is caused by the electronic properties of the adsorbed molecule, namely, the electronegativity parameter

$$\psi = \frac{I + A}{2},$$

where I is the ionisation potential and A is the electron affinity.

Subsequent studies covered a much wider range of organic molecules of various nature with a very wide range interval of electronegativities (Table 1).^{211–214} Thin vanadium and indium films (~ 10 nm thick) with $T_c = 2.4$ and 4.1 K, respectively, were used as superconductors. The films were obtained by vapour deposition of the pure (99.999%) metals in a high vacuum (10^{-6} Pa) onto a single-crystal quartz substrate. The molecules of organic compounds, mainly those with planar structures, were deposited on the films by evaporation *in vacuo* or by chemical methods. The superconducting transition temperatures and the critical currents before and after the adsorption were determined by the contact resistance method. For a vanadium film, good correlation was observed between the electronegativity and the sign of the T_c change upon adsorption of 14 different organic compounds. Adsorption of electron-donating molecules (anthracene, tetracene, perylene, *etc.*) with low electronegativity ($\psi \approx 3.9$ eV) caused an increase in T_c . Conversely, electron-acceptor molecules, for example, tetracyanoquinodimethane with $\psi \geq 5.5$ eV, decreased the T_c . Similar regularities were also noted for an indium film.

However, there are exceptions. For example, the superconducting transition temperature increased upon deposition of

Table 1. Changes in T_c upon adsorption of organic compounds on low-temperature metallic superconductor films and certain physicochemical parameters of these compounds.²¹⁴

Adsorbed compound	T_c /K	ΔT_c /K	I /eV	A /eV	ψ /eV
Thin vanadium film					
Anthracene	2.33	+0.10	7.23	0.42	3.83
Tetracene	2.76	+0.075	6.88	1.0	3.94
Perylene	2.92	+0.08	7.15	0.85	4.0
Phenothiazine	2.20	+0.09	7.28	—	—
TMP	2.45	+0.09	8.65	—	—
2-Aminoanthraquinone	2.62	+0.06	<9.34	<0.5	<4.9
1,4,5,8-Tetrachloro-anthraquinone	2.23	+0.025	>9.34	0.66	>5.0
Pyromellitic dianhydride	2.25	−0.11	—	0.85	—
TCQDM	2.25	−0.10	—	1.7	>5.5
Tripyridyl-s-triazine	3.6	+0.05	—	—	—
Titanium dicyclopentadienyl dichloride	2.42	−0.05	—	—	—
Thin indium film					
TMP	4.1	0.00	8.65	—	—
TCQDM	4.09	−0.23	—	1.7	>5.5

Note. TMP is 3,4,7,8-tetramethyl-1,10-phenanthroline; TCQDM is tetracyanoquinodimethane.

electron-accepting tripyridyl-*s*-triazine molecules on a vanadium film. The electron-donating TMP molecules affected vanadium and indium films differently: the adsorption of TMP on the vanadium film increased T_c , whereas that on the indium film did not change T_c .²¹⁴ This was explained by the formation of a 'metal atom – organic molecule' complex. In the case of vanadium, which is a transition metal, a bond is formed between an unoccupied *d* orbital and a molecular π orbital of the organic molecule; this favours the transfer of an electron to the superconductor film and hence changes its superconductivity. Unlike vanadium, indium does not have a similar *d* orbital, therefore TMP adsorption does not affect its properties.

In yet another work,²¹⁴ the effects of the adsorption of organic compounds on the critical current of superconducting films was also studied. The adsorption of electron donors, *viz.*, tetracene and perylene, on a vanadium film resulted in an increase in the critical current. Although a rather good correlation exists between the electronegativity of organic molecules, ψ , and the critical parameters of superconductivity of the vanadium film, I_c and T_c , the detailed mechanism of this phenomenon remains unclear. This can be due to charging of the superconducting film surface upon adsorption of organic compounds. For example, it was shown²¹⁵ that the superconducting transition temperature of an indium film depends on the surface charge sign. A strong acceptor, TCQDM, 'withdraws' electrons from the superconductor bulk, the concentration of the charge carriers decreases, and T_c decreases by 0.23 K. A decrease in T_c was also observed in an external electrical field where the film surface was charged positively.

With the advent of oxide-based HTSC materials, research into the effect of adsorption of organic compounds on the critical parameters of superconductivity has gained new impetus. An organic dye, octaethylporphyrin, was applied onto a plate 3 mm long and 50 μm wide made of a 100 nm thick $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film on a MgO (100) single crystal substrate.²¹⁶ After cooling the specimen below T_c , the superconductor was irradiated, and the dependence of the current on the wavelength of incident light was measured. The system response to the light and the wavelength selectivity were much more significant at temperatures below T_c . The strongest response estimated as the current passing through the plate was observed at a wavelength of 600 nm corresponding to the maximum absorption of the dye.

The effect of a deposited conducting polymer, polypyrrole, on superconductivity of an $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film was studied.²¹⁷ The electric conductivity of the film at temperatures higher than T_c , as well as the T_c itself, depend on the electric properties of the polymer. The dielectric polymer little affects the electric properties of the film. The polymer in the conducting or oxidised forms decreases T_c of the superconducting film by 15 K. Chemical or electrochemical reduction of the polymer results in restoration of the original T_c value. In order to explain these phenomena, the authors put forward two assumptions: (1) the polymer in the oxidised state does not affect the concentration of weakly bound oxygen in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film, and hence the change in T_c is not related to oxygen; (2) the observed change in T_c is caused by the 'proximity' effect, *i.e.* partial penetration of the Cooper pairs into the conducting polymer layer.

In continuation of these experiments, temperature dependences of the contact resistance at the boundaries between the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{1.6}\text{Ca}_{2.4}\text{Cu}_3\text{O}_{10}$ HTSC ceramics, on the one hand, and the oxidised form of a deposited conducting polymer, poly(3-hexylthiophene), on the other hand, were studied.²¹⁸ The electric resistance of this contact decreases around T_c . It was assumed that ceramics in the superconducting state can induce a kind of superconductivity in the polymer, in other words, this phenomenon can be directly related to the 'proximity' effect.

Exposure of an $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ powder to organic donor-acceptor electron-transport (DAET) systems (for example, $\text{DMF}-\text{CCl}_4$, 2,2'-bipyridyl-monoethanolamine, $\text{DMSO}-\text{CCl}_4$, *etc.*) was accompanied by partial etching of the ceramic without

considerable change in its phase composition.^{219,220} Etching removes the labile near-surface oxygen and exposes the more perfect structured layers; the contact between the granules and their ability to sinter are improved. The concentration of oxygen in the material bulk does not change. Thus, etching of HTSC ceramics powder with DAET-systems under mild conditions results in modification of the surface layers of the species and is accompanied by stabilisation of the superconducting state and improvement of the superconductor quality.

Room-temperature treatment of an $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ powder with an excess of 1-hydroxy-2,2,6,6-tetramethylpiperidine (HTMP), which is readily oxidised into a stable nitroxyl radical even on treatment with atmospheric oxygen, is accompanied by extraction of weakly bound oxygen from the specimen bulk.²²¹ An EPR study of the radical accumulation kinetics made it possible to determine the amount of the oxygen extracted and to estimate the activation energy of this process. The determined activation energy, $\sim 16 \text{ kJ mol}^{-1}$, is comparable with E_a for the diffusion of highly reactive oxygen in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. It is much smaller than the values that characterise the evolution of weakly bound oxygen to the gas phase upon thermal desorption (at $x < 0.006$, $E_a = 120 \text{ kJ mol}^{-1}$). Apparently, this difference can be explained by the fact that HTMP adsorbed on the ceramic lowers the activation barrier for oxygen exit from the surface layer of the specimen. As the weakly bound oxygen is extracted, the superconductivity is impaired and disappears completely if more than 0.03 a.u. of oxygen is lost. Since a rather small change in the oxygen content cannot cause such a strong degradation of the superconductor, the actual major role is probably played by the magnetic moment of stable nitroxyl radicals formed during HTMP oxidation (see below). In another study,²²² the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic was converted into a metastable state by mild removal of oxygen from the O(4) position (see Fig. 1*b*) at 523 K using a different organic reducing agent, namely, azobenzene. The type of the kinetic dependence for oxygen removal from the Cu(1) layers allows one to assume that it involves the diffusion mechanism. The dynamics of the change in the crystal lattice parameters *a*, *b* and *c* depending on the oxygen concentration was followed. Subsequent treatment of the ceramic with iodine resulted in restoration of the lattice parameters to the original values (*i.e.* to those before the reaction with azobenzene).

Treatment of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ with methanol²²³ containing $\sim 20 \text{ mass } \%$ of HTMP and 10% KOH as an HTMP oxidation catalyst²²⁴ was also accompanied by extraction of weakly bound oxygen from the ceramics. The superconductivity parameters of the ceramics after this treatment strongly depended on their initial properties and on the methods of preparation. The superconductivity parameters of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ specimens obtained by cryochemical technology (A) and by self-propagating high-temperature synthesis (B) changed essentially upon contact with HTMP and KOH in methanol at 313 K for 120 min. The superconducting transition temperature of the specimen A decreased strongly (to 60 K). This was explained²²³ by removal of reactive oxygen from the O(4) and O(5) positions of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ crystal lattice. The specimen B displayed no trend to form a phase with $T_c = 60 \text{ K}$, and the change in its superconducting transition temperature was smaller. This phenomenon is due to the specifics of structural transformations on the ceramic's surface, which hinder oxygen diffusion from the specimen bulk.^{225,226} These transformations were not observed in the oxygen extraction from the $\text{Bi}_2\text{Sr}_2\text{CaCu}_3\text{O}_{8+x}$ ceramic, and the superconductivity was suppressed completely. However, brief treatment with HTMP (15 min) increased the superconducting transition temperature by 13 K. It should be noted that a similar phenomenon was observed upon removal of a small amount of oxygen ($x \approx 0.03$) from the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ ceramic.^{227–230} This is probably due to the extraction of the highly reactive oxygen intercalated between the $\text{BiO}-\text{O}(\text{Bi})$ layers and the essential increase in the unit cell parameter *c*. Prolonged treatment

did not change T_c , but the fraction of the superconducting phase decreased to complete loss of superconductivity.

The much weaker effect of treatment with methanol containing 10% KOH on the specimen A than on the specimen B was explained by the higher oxidising and catalytic activity of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic obtained by self-propagating high-temperature synthesis.²³¹ The extraction of oxygen from $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ was accompanied by an insignificant decrease in the fraction of the superconducting phase and, as in the previous case, an increase in the superconducting transition temperature by 11 K. The difference between the effect of the 10% KOH solution in methanol and the effect of the HTMP solution in methanol is due to the fact that methanol cannot react with the weakly bound oxygen responsible for the material superconductivity.

In one of the first studies on the chemical modification of HTSC material surfaces,²³² various ferrocene derivatives containing aminoalkyl, aminoaryl, thiol, phosphino, amide and hydroxymethyl functional groups were adsorbed at room temperature onto the surfaces of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic and thin film from a solution in acetonitrile. The solution concentration of the reagents was 10^{-3} mol litre $^{-1}$. It was shown by cyclic voltammetry that only molecules containing aminoalkyl, aminoaryl and thiol groups are adsorbed. This implies that preferential adsorption occurs on the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ surface. Ferrocenes containing such substituents as amide, phosphino and hydroxymethyl groups are virtually not adsorbed on HTSC materials. The pronounced ability of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ to adsorb amino groups is explained by the presence of the Cu(II) and Cu(III) ions on its surface. The adsorption of ferrocene derivatives with thiol groups is explained by the high oxidising ability of the superconducting material, on the one hand, and by the reducing properties of thiol groups, on the other hand. Treatment of thin $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ film with solutions of various ferrocene derivatives in acetonitrile for 3 h at room temperature did not affect its superconductivity. An increase in the treatment time to 48 h decreased T_c by 2 K. It was noted that covering of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ surface with a monolayer of molecules of substituted ferrocenes makes the HTSC material resistant against moisture.

Cyclic voltammetry was used to study the effect of small amounts of water on the adsorption of 11-mercaptoundecanoyl-ferrocene (MUF) on the surface of the $\text{Ti}_{1.4}\text{Ba}_2\text{CaCu}_2\text{O}_z$ ceramic.²³³ The presence of 5% water in a 0.1 M solution of MUF in acetonitrile decreased considerably the degree of coverage of the ceramic's surface with MUF molecules. If ethanol was used as the solvent, adsorption virtually did not occur. However, adsorption of MUF from dehydrated solvents gave a dense and stable monomolecular layer of chemisorbed MUF. It is believed that water affects adsorption due to a BaCO_3 layer formed as a result of corrosion, which does not adsorb MUF.

Direct proof of the chemical interaction between the amino groups and the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ surface was obtained in studies using Raman spectroscopy.²³⁴ It was shown that 4-aminopyridine molecules are chemisorbed on the superconductor surface to form a dense monomolecular layer of vertically arranged molecules; the amino group is coordinated with the surface copper atoms of the superconductor (Fig. 7).

A small review of the early studies on the adsorption of organic molecules on HTSC materials²³⁵ presented data on the chemisorption of ferrocenes containing various ligands, on the Raman spectra of monomolecular layers on HTSC material surface and on the kinetics of adsorbent-adsorbate exchange. Special attention was given to the practical use of HTSC materials modified with adsorbed organic molecules. For example, monolayer adsorption of hydrophobic molecules on HTSC materials can be used to prevent their corrosion in a humid atmosphere. In addition, this treatment increases considerably the adhesion between the polymer and the HTSC material. Superconductors coated with a monolayer of organic molecules can serve as the basis for obtaining synthetic tunnelling contacts used in super-

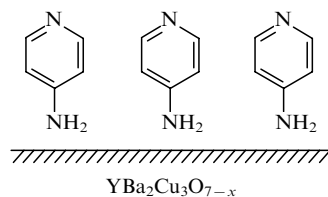


Figure 7. Coordination of adsorbed 4-aminopyridine molecules on the surface of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ HTSC ceramic.²³⁴

conducting quantum interferometer probes. They can also be useful for solving a number of fundamental problems of the physics of HTSC materials.

Adsorption of naphthalene on the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic was accompanied by an increase in T_c and the transport critical current.²³⁶ The treatment was carried out by immersion of samples in chloroform solutions of naphthalene of different concentrations. According to gravimetric data, this treatment results in covering of the surface of the samples with a shell of naphthalene molecules from one to several hundred monolayers thick. The transport critical current was measured with a vibrating magnetometer using a ring cut from the ceramic under study; the superconducting transition temperature was determined by recording the real part of magnetic susceptibility. Adsorption of naphthalene from 0.2 M solution in chloroform did not affect the critical superconductivity parameters of the specimen. An increase in the naphthalene concentration to 1 mol litre $^{-1}$ increased the T_c by 1.5 K. Further increase in the naphthalene concentration did not change T_c considerably. For example, the T_c increase due to treatment of the specimen with a saturated solution (3.5 mol litre $^{-1}$) was 1.62 K. If naphthalene is washed off from the specimen with pure chloroform, the original superconducting transition temperature was restored almost completely (Fig. 8).

It has to be noted that the absolute value of the signal amplitude χ' did not depend on the treatment of the specimen. Hence, naphthalene adsorption does not change the fraction of the superconducting phase in the specimen. The transport critical current after naphthalene adsorption from a saturated solution increased by 20%. Additional experiments on measurements of the total current decay in a superconducting ring were carried out in order to analyse this interesting phenomenon. It was found that treatment of a specimen with naphthalene does not affect the decay rate and hence does not affect the pinning energy of the Josephson vortices.

The mechanism of the effect of adsorbed naphthalene on superconductivity has not been determined so far. Probably, a bond between an unoccupied d orbital of the Cu(III) ion in the superconductor and the molecular π orbital of naphthalene is

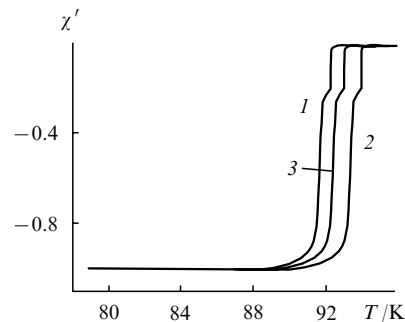


Figure 8. Temperature dependence of the real part (χ') of magnetic susceptibility of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic;²³⁶ (1) original specimen; (2) after treatment with saturated solution of naphthalene in chloroform; (3) after washing the treated specimen with pure chloroform.

formed, which favours electron transfer to the superconductor and hence changes its properties.

The change in the superconducting transition temperature caused by the naphthalene adsorption cannot be explained by donor-acceptor interactions, since interactions of electron donors with superconductors having hole-type conductivity most probably decrease the concentration of the charge carriers and hence decrease rather than increase T_c . The increase in T_c observed in the experiment is probably determined by the effective charging of the superconductor granule surfaces upon adsorption of naphthalene molecules.²³⁷

As shown above, the effect of adsorption of organic molecules on the properties of HTSC materials primarily results from donor-acceptor interactions or redox reactions involving copper and oxygen ions. On the other hand, the high sensitivity of the critical parameters of superconductivity to external magnetic field provides a reason to assume that the superconductor properties are strongly affected by paramagnetic species, *i.e.*, radicals possessing magnetic moments.

The effect of adsorption of a stable nitroxyl radical, 2,2,6,6-tetramethylpiperidin-*N*-oxyl (TEMPO), on the transport properties of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconducting ceramic was studied.^{238, 239} Adsorption was carried out at room temperature by immersing the ceramics in a 0.2–2.0 M chloroform solution of TEMPO. The specimen was kept in the solution for 12 h and dried in air. The critical current was measured as a function of temperature using a vibrating magnetometer. In reference experiments, the specimens kept in pure chloroform for 30 days did not show any effect of chloroform on the ceramic's properties. The superconducting transition temperature was measured by recording the magnetic susceptibility on an alternating current magnetometer. Figure 9 shows the dependences of the transport current I_c on temperature at various radical concentrations in the starting solution. It is evident that radical adsorption affects rather strongly the critical current in the temperature range from 77.4 to 86 K. At a content of adsorbed radicals in the ceramic equal to 1.7×10^{-2} mass %, the critical current was higher than that in the original non-treated specimen over the entire temperature range studied. Further increase in the content of radicals decreased I_c (see Fig. 9). The superconducting transition temperature of the ceramic before and after adsorption of radicals remained the same.

The mechanism of the effect of adsorbed molecules with their own magnetic moments on superconductivity is probably rather complicated. The results of additional experiments carried out specially to reveal the characteristic features of this effect were analysed within the framework of the intergranular conductivity

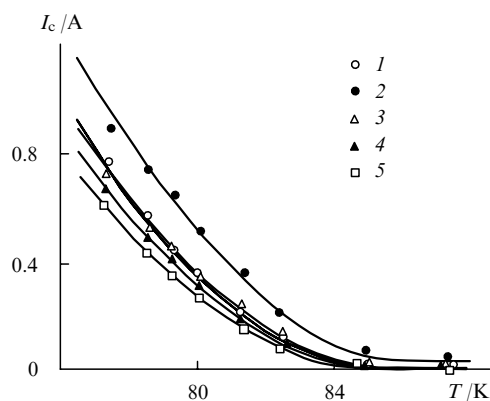


Figure 9. Temperature dependence of the critical current in the $\text{TEMPO}_y\text{-YBa}_2\text{Cu}_3\text{O}_{7-x}$ composite material at the following concentrations of the stable radical: 0 mass % (1), 1.7×10^{-2} mass % (2), 4.2×10^{-2} mass % (3), 8.5×10^{-2} mass % (4), 1.7×10^{-1} mass % (5).^{238, 239}

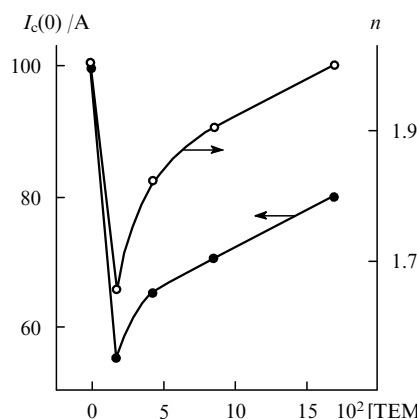


Figure 10. Dependence of the critical current extrapolated to 0 K and the exponent n in the Eqn (3) on the concentration of stable radicals TEMPO in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic.^{238, 239}

model.²⁴⁰ The general temperature dependence of the critical current for various contacts between the granules has the form

$$I_c(T) = I_c(0) \left(1 - \frac{T}{T_c}\right)^n, \quad (3)$$

where $I_c(0)$ is the critical current obtained by extrapolation to 0 K; n is an index reflecting the nature of contacts between the granules, which can vary from 1 to 2. Figure 10 presents the calculated dependences of the critical current $I_c(0)$ and the index n on the concentration of radicals.^{238, 239} It is evident that n is equal to 2 in the absence of radicals and $n < 2$ at their low concentrations. This means that upon adsorption of a radical, an SNS contact is transformed to an SNINS contact, or, in other words, the intergranular bond is improved and approaches a character close to the classical Josephson transition.²⁴⁰ On the other hand, the absolute value of the critical current also decreases, apparently due to the effect of the radical magnetic field on the intergranular bond. If the radical concentration is increased further, n eventually becomes equal to two. The change in the intergranular conductivity correlates with the change in the critical current $I_c(0)$. The increase in the latter at high radical concentrations is probably due to a specific behaviour of the highly concentrated magnetic media. For example, it is known that at a concentration of paramagnetic species above a certain value a significant change in the spin orientation is observed and the total magnetic moment of the medium decreases. Hence, in our case the increase in the concentration of stable radicals should weaken the effect of the magnetic moments on the conductivity of the intergranular layer, which is confirmed experimentally.

A study of the transport properties of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ HTSC ceramic upon magnetic field trapping by granules of the specimen showed that an increase in the critical current between the granules is actually observed at certain parameters of the magnetic field 'uptaken' by the granules.²⁴² Moreover, treatment of a superconducting ceramic ring with stable radicals does not change the decay rate of the current induced in the ring. Hence, additional pinning centres are not formed, and probably the increase in the transport critical current in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic after adsorption of stable radicals mostly occurs due to 'uptake' of magnetic field of a radical in the specimen granules. It was shown experimentally²⁴¹ that interaction of the Josephson and Abrikosov vortices can increase the critical current essentially. An effect on the intergranular bonding and the donor-acceptor properties of the stable radical, which probably manifests itself as a change in the index n in Eqn (3), cannot be ruled out either. However, the major role still belongs to the 'uptake' of the radical magnetic field into the specimen granules.

The critical parameters of superconductivity of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic containing adsorbed radicals depend on

the temperature to which a specimen has been cooled prior to the measurements.²⁴³ The type of the temperature dependence of magnetic susceptibility indicates an increase in the critical parameters of superconductivity upon cooling of the specimen. The explanation for this is that at lower temperatures, greater magnetic flux from the radical molecules is 'uptaken' by the granules, resulting in an increase in the critical parameters.

The effect of the adsorption of a stable diphenylpicrylhydrazyl radical (DPPH) on the superconductivity of the $\text{Bi}_{1.8}\text{Pb}_{0.5}\text{Sr}_{1.9}\text{Ca}_{2.5}\text{Cu}_{3.2}\text{O}_z$ ceramic was studied.²⁴⁴ Before an experiment, the surface of the specimen to be studied was freed from adsorbed water, CO_2 and organic contaminants by calcination in an oven at 473 K *in vacuo* for one hour. Then the cleaned specimen was transferred into a glass tube containing DPPH powder and sealed. The adsorption of DPPH was carried out by heating the tube to 473 K for 20 min. After that, the tube was broken, and the specimen was transferred into a cell for measurement of magnetic properties. For reference purposes, the procedure described above was also carried out in the absence of DPPH. The superconductivity parameters of the specimen under study were measured with an alternating current magnetometer. Figure 11 presents the temperature dependence of the magnetic susceptibility of the $\text{Bi}_{1.8}\text{Pb}_{0.5}\text{Sr}_{1.9}\text{Ca}_{2.5}\text{Cu}_{3.2}\text{O}_z$ ceramic. It is evident that upon adsorption of the radical, the curve shifts towards the low-temperature region; this indicates that the current-carrying ability of the specimen decreases. Thermal treatment of the ceramic also deteriorates superconductivity, but in this case the change is much less. The experimental values of magnetic susceptibility were compared with the real part of the magnetic susceptibility calculated within the framework of the simple Kim model.²⁴⁵ Good agreement between the experimental results and the calculations were achieved with the assumption that the intergranular layer is affected by a static magnetic field of 0.13 mT (see Fig. 11, curve 2).

Given the magnetic induction B , one can estimate the distance d between an adsorbed radical molecule and an intergranular contact:

$$d = \left(\frac{2\mu}{B} \right)^{1/3}, \quad (4)$$

where $\mu = g\beta S$ is the magnetic moment of the radical, $g = 2$ is the g -factor of a free electron, β is the Bohr magneton, $S = 1/2$ is the spin quantum number. Substituting the above value of $B = 0.13$ mT in the formula (4), we obtain $d = 5.6$ nm. This distance is in good agreement with the thickness of the non-superconducting layer, which is generally located on the superconductor surface and is estimated as 3–5 nm.²⁴⁶ Such consistency supports the suggested model of the effect of the magnetic

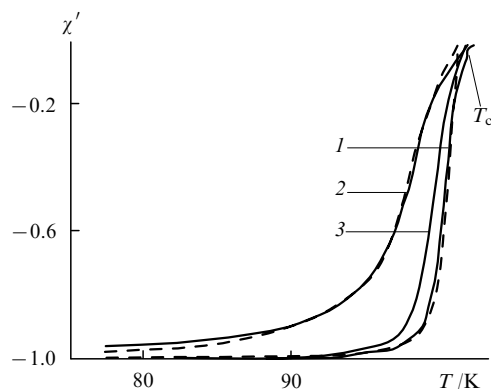


Figure 11. Temperature dependence of magnetic susceptibility of the $\text{Bi}_{1.8}\text{Pb}_{0.5}\text{Sr}_{1.9}\text{Ca}_{2.5}\text{Cu}_{3.2}\text{O}_z$ ceramic;²⁴⁴ (1) original specimen; (2) after adsorption of the DPPH radical; (3) after heating in a sealed tube for 1 h. Solid lines — experiment, dashed lines — calculated real part of magnetic susceptibility within the simple Kim model.

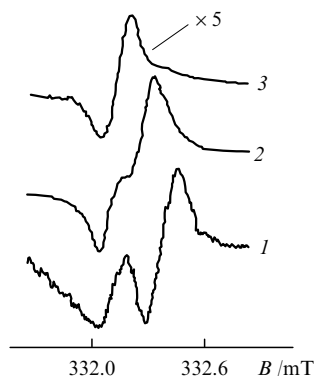


Figure 12. EPR spectra of the DPPH radical adsorbed on the surface of the $\text{Bi}_{1.8}\text{Pb}_{0.5}\text{Sr}_{1.9}\text{Ca}_{2.5}\text{Cu}_{3.2}\text{O}_z$ superconducting ceramic recorded at the temperatures: 77.4 (1), 89 (2) and 125 K (3).²⁴⁴

field of adsorbed radicals on the intergranular current in superconducting ceramics.

The EPR spectrum of the DPPH radical adsorbed on the surface of the $\text{Bi}_{1.8}\text{Pb}_{0.5}\text{Sr}_{1.9}\text{Ca}_{2.5}\text{Cu}_{3.2}\text{O}_z$ ceramic in superconducting state at 77.4 K consists of two lines (Fig. 12). As the specimen is heated, the high-field line of the doublet starts to shift downfield and, since the position of the low field line remains unchanged, splitting decreases. At 125 K, *i.e.*, at a temperature above T_c , the high-field line coalesces with the low-field one, and a singlet corresponding to the line in the EPR spectrum of the DPPH radical remains. It follows that the low-field line of the doublet, the position of which is not changed, corresponds to the adsorbed radical located at a great distance from the superconducting phase. For this reason, this phase does not affect the low-field line. The shift of the high-field line with the increase in temperature can be caused by the following reasons. First, the magnetic flux trapped by granules of a superconducting specimen (the Abrikosov vortices) located in an external magnetic field with $B_0 \approx 0.33$ mT changes the magnetic field parameters in the vicinity of the adsorbed radical. Second, the magnetic moment of the adsorbed radical has a 'mirror' image in the diamagnetic surface of the superconducting specimen, and probably the line position in the EPR spectrum of the radical is actually determined by the magnetic field of this 'mirror' dipole.

2. Intercalation of organic molecules into the crystal structure of high-temperature superconducting materials

A characteristic feature of HTSC materials is their layered structure which plays an important role in the transition to the superconducting state. As noted above and as has been shown by Bulaevskii,²⁴⁷ intercalation of atoms and molecules into the structure of layered solids changes essentially their chemical and physical properties. For example, intercalation of pyridine molecules into the TaS_2 superconductor was accompanied by a significant increase in the superconducting transition temperature (from 0.5 to 4.5 K).²⁴⁸ Hence, one can expect that intercalation of organic molecules in an HTSC material would affect strongly the critical parameters of superconductivity. It was even suggested that intercalation of organic molecules in layered inorganic materials can result in superconductors with high critical temperatures.²⁴⁹

Bismuth oxide- and thallium oxide-containing superconductors can be suitable objects for studying the effect of intercalation on superconductivity. In fact, the magnetic properties of the $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_z$ ceramic with $T_c = 105$ K underwent interesting changes on treatment with benzene.²⁵⁰ A powder with a particle size of ~ 50 μm obtained by grinding bulk ceramic specimens was placed in benzene and kept at room temperature for a period from 10 min to 2.5 h. Then benzene was evaporated at 308 K, and the powder was placed in molten paraffin in order to

prevent electrical contact between the granules. As a rule, the specimens obtained by this method manifested weak paramagnetism with an absolute susceptibility of 10^{-7} or ferromagnetism with a magnetisation of 10^{-9} A m² g⁻¹.

Specimens of the ceramic that had been kept in benzene for 20–30 min had unusual electrophysical properties. First, rather high diamagnetic response was recorded at room temperature and hysteresis phenomena were observed in low magnetic fields. For example, the magnetisation in a field of 10 mT at 300 K was 8×10^{-6} A m² g⁻¹. Second, a stepwise change in the external magnetic field was accompanied by magnetisation relaxation. Third, if the temperature of the specimen was cycled in the range from 77.4 to 300 K, the initial magnetisation decreased gradually. For example, the maximum magnetisation of a specimen was 2×10^{-5} A m² g⁻¹ after the first cooling, whereas it was as low as 8×10^{-6} and 4×10^{-6} A m² g⁻¹, respectively, after the second and third cooling. Fourth, the EPR spectrum of the specimen at 300 K contained a low-field microwave absorption signal. Repeated cyclic changing of the specimen temperature decreased this signal. X-Ray diffraction analysis revealed additional reflections, apparently due to a new phase that was formed in the specimen. Such unusual physical properties of the Bi_{1.7}Pb_{0.3}Sr₂Ca₂Cu₃O_z ceramic containing intercalated benzene can be a manifestation of superconductivity. Therefore, the authors of this study²⁵⁰ believed that they could detect a small fraction of a superconducting phase in a specimen at room temperature. Unfortunately, the phenomena described above were only observed on some specimens. They could not be reproduced in other specimens, and the fraction of the superconducting phase could not be increased by varying the treatment conditions.

Later, a detailed study of the intercalation of planar aromatic molecules into superconducting ceramics was undertaken.²⁵¹ Intercalation of benzene and phthalocyanine complexes of copper and nickel into bismuth-containing ceramics, Bi₂Sr₂CaCu₂O_z and Bi₂Sr₂Ca₂Cu₃O_z, and into a thallium-containing ceramic, Tl₂Ca₂BaCu₂O_z, were carried out in sealed tubes at 273–423 K. As in yet another study,²⁵⁰ the ceramics studied displayed unusual physical properties at room temperature: the specimens retained magnetisation for some time after the external magnetic field was turned off; a low-field microwave absorption signal was observed; the magnetisation curves had unusual shapes; negative magnetisation was recorded in low magnetic fields (1–2 mT). X-Ray diffraction and Raman spectroscopic data showed that these organic compounds were located between the Tl–O or Bi–O double layers (see Fig. 1 c).

Intercalation of zinc and nickel phthalocyanine complexes also affected the properties of bismuth- and thallium-containing HTSC ceramics. In Ref. 252, as in previous studies,^{250, 251} unusual physical properties of these ceramics at room temperature were reported. For example, at 300 K the magnetisation of a metal phthalocyanine intercalated in the ceramics was found to be anomalously high, two orders of magnitude higher than the magnetisation of a free metal phthalocyanine complex. In the superconducting state (at 90 K), the magnetisation of the ceramics with the intercalated complex was one order of magnitude smaller and was equal to 10^{-2} A m² g⁻¹. The temperature dependence plots of the magnetisation of (NiPc)_{0.1}Bi₂Sr₂CaCu₂O_z and (NiPc)_{0.09}Tl₂Ca₂BaCu₂O_z specimens (Pc = C₃₂H₁₆N₈) obtained on cooling in magnetic fields and without a field showed noticeable differences starting from 250 K. Such unusual magnetic properties can indicate that the specimens display superconductivity at rather high temperatures. Certain assumptions on the nature of the observed phenomena were made.^{250–252} It was assumed that molecules of aromatic compounds characterised by strong electron delocalisation form new composite materials when introduced into the structure of a layered superconductor. These materials manifest unusual physical properties which resemble in certain respects the properties of superconductors; this is primarily due to the possible formation of quasi-species — ‘anyons’ with

half-integer statistics. It was shown theoretically²⁵³ that similar quasi-species present in two-dimensional electronic systems can generate a superconducting state, the transition to which occurs by a mechanism different from the generally accepted one and which is characterised by a higher T_c .

In addition, the superconductivity of intercalated composites can be explained using the exciton mechanism.²⁵⁴ In fact, intercalation of organic molecules into layered crystal systems results in ‘sandwiches’ that consist of alternating thin metal layers and dielectric intermediate layers. An electron–hole pair (exciton) can be formed in such systems. High magnetisation of intercalated bismuth- and thallium-containing HTSC oxides can also be due to the joint orbital contribution of π -electrons of aromatic molecules, which can form two-dimensional conducting layers due to the structural features of the material. According to X-ray diffraction data,²⁵² intercalation changes the material structure substantially. Not only do the distances between the structural Tl–O and Bi–O layers change, but also those between the atoms along the *a* and *b* axes (see Fig. 1 c). These transformations affect the electronic condition of the copper ion and result in transition from the usual phase with antiferromagnetic ordering of the copper spin states to the ferromagnetic phase. The effect of the amount of the metal phthalocyanine intercalated in the ceramics on this process was observed for the (NiPc)_yBi₂Sr₂CaCu₂O_z system.²⁵²

V. The effect of superconductivity on the electronic state of the adsorbed molecules and on adsorption processes

The effect of the substrate superconductivity on the fluorescence lifetime of an adsorbed dye, 1,4-bis(5-phenyloxazol-2-yl)benzene (POPOP), was studied.²⁵⁵ Adsorption of the dye on a YBa₂Cu₃O_{7–x} ceramic substrate was carried out by treating the specimen with a 10^{-3} M POPOP solution for 100 s in toluene followed by drying in air. As a result of this treatment, the width of the superconducting transition temperature of the substrate, $\Delta T = 1$ K, expanded to $\Delta T = 8$ K towards low temperatures. The fluorescence lifetime τ at each particular temperature was calculated using an exponential kinetic curve of the decay of the dye fluorescence excited by light with a wavelength of $\lambda = 330$ nm. Figure 13 presents the temperature dependences of the relative specific resistance of the substrate (ρ/ρ_{298} , where $\rho_{298} = 2 \times 10^{-3}$ Ω cm is the substrate specific resistance at 298 K) and the lifetime of fluorescence of adsorbed POPOP (τ). If temperature is decreased, an abrupt increase in τ is observed in the region of transition into the superconducting state. In control experiments, where the fluorescence lifetime of POPOP molecules adsorbed on a non-superconducting substrate with similar com-

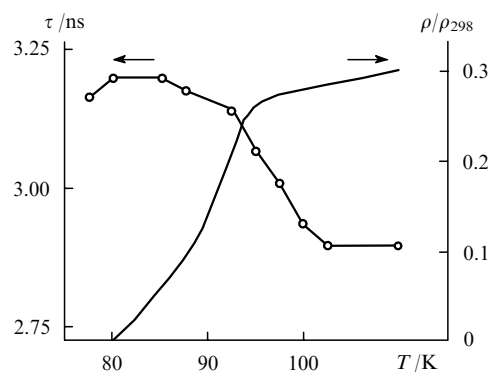


Figure 13. Temperature dependences of the relative specific resistance of the YBa₂Cu₃O_{7–x} support and the fluorescence lifetime of POPOP adsorbed on this support.²⁵⁵

position was measured, no such dependence of τ on temperature was observed.

Thus, the abrupt increase in the lifetime of the electronically excited singlet state of POPOP upon temperature decrease is due to the specific features of the superconducting state of the substrate. Probably, the following aspects are most important. First, the transition of the ceramic in the superconducting state is accompanied by small structural changes of its crystal lattice,^{256, 257} which can affect the geometry of the adsorbed molecule and thus change the lifetime of the excited electronic state. Second, the transition into the superconducting state changes the dielectric constant of the surface layer of the HTSC material;²⁵⁸ this results in a change in the electric field strength near the surface and hence can affect the probability of nonradiative transitions of the excited molecules of the adsorbate. Third, the transition of the substrate in the superconducting state can weaken the interaction of the electronically excited adsorbate molecule with the conductivity electrons of the substrate, which also affects the luminescence lifetimes.

The effect of the substrate superconductivity on the electronic state of the adsorbed molecule was observed:²⁵⁸ the fluorescence quantum yield of an organic dye, erythrosine, adsorbed on a superconductor surface changed in a stepwise manner at the superconducting transition temperature of the substrate. A bulk ceramic specimen of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ($T_c = 87$ K), an epitaxial polycrystalline film of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ($T_c = 50$ K) and a low-temperature superconductor film of NdN ($T_c = 13.5$ K) were used as the superconductors. The fluorescence quantum yield of erythrosine applied on the low-temperature superconductor NdN underwent a small (5%) stepwise change at T_c , while the quantum yield above and below this point virtually did not depend on temperature. A different behaviour was observed where the dye was adsorbed on HTSC substrates. The fluorescence quantum yield of erythrosine adsorbed on a $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ polycrystalline film increased by 100% as the latter has passed in the superconducting state. The quantum yield of erythrosine adsorbed on the bulk $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramic changed substantially around the temperatures of 50 and 90 K, which correspond to two superconducting subsystems, *viz.*, the intergranular layers and granules, respectively. The conclusion was made²⁵⁸ that the fluorescence quantum yield of the dye changes upon transition of the adsorbate in the superconducting state owing to the change in the dielectric constant of the material.

An original way for the separation of diamagnetic and paramagnetic molecules on a porous membrane made of a superconducting material, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, was reported.²⁵⁹ In the superconducting state, the porous ceramic is 'transparent' for nitrogen molecules but does not pass the paramagnetic molecules of oxygen. The O_2 : N_2 concentration ratio decreased by a factor of six after a gas mixture (air) has passed through such a membrane. There was no gas separation effect with a non-superconducting membrane at the same temperatures, which is explained by high (comparable with the energy of thermal movement of molecules) energy of interaction between the magnetic moment of a triplet oxygen molecule and its mirror image in the superconducting surface of the membrane material. As a result, the effective cross-section of interaction of the oxygen molecule with the superconductor increases and a paramagnetic oxygen molecule penetrates the membrane with greater difficulty than a diamagnetic nitrogen molecule.

The features of interaction of HTSC materials with charged or magnetoactive species provide the possibility of using these materials for practical purposes. For example, the focusing of electron and ion beams passing through a superconducting tube made of HTSC ceramics was identified and studied.^{260–262} A theoretical estimate²⁶⁰ of the focusing effect of a superconducting surface on the beam of free electrons or ions showed that at certain velocities of the beam the focusing force can be comparable to, or even exceed, the force of Coulomb repulsion of the charged species in the beam. The vast experimental and theoretical material that

has been accumulated shows the possibility of using HTSC materials for these purposes.²⁶¹ For example, the passage of an electron beam through a superconducting tube from bismuth-containing ceramics with $T_c = 105$ K was studied experimentally:²⁶² an electron beam with an energy of 340 keV, an intensity of 0.8 kA and a diameter of 8 mm was directed into a superconducting tube. The electron beam leaving the tube was focused to a diameter of 1.1 mm.

The authors of the present review have thoroughly studied the interaction of a superconductor with magnetoactive species.^{263, 264} Specific features of the low-temperature adsorption and desorption of oxygen and argon on a 0.25–0.50 mm fraction of powder of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconducting ceramic were studied. The adsorption isotherms of argon and oxygen in the temperature range from 77.4 to 98 K were obtained.

The desorption curves coincided completely with the adsorption curves. Hence, the adsorption of argon and oxygen on the oxide $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is reversible and can be regarded as physical adsorption. The experimental isotherms of the argon and oxygen adsorption in the entire temperature range studied correspond to the 'second type'²⁶⁵ and are well described by the BET polymolecular adsorption theory.²⁶⁶ The temperature dependence of the superconducting adsorbent specific surface calculated using the BET equation for oxygen adsorption differs essentially from the similar dependence obtained for argon adsorption (Fig. 14). According to the BET theory, the geometrical dimensions of the surface do not depend on temperature and are determined by the nature of the material. This assumption is totally consistent with the low-temperature adsorption of argon. The specific surface of the specimen measured with respect to argon was found to be $1.05 \text{ m}^2 \text{ g}^{-1}$.

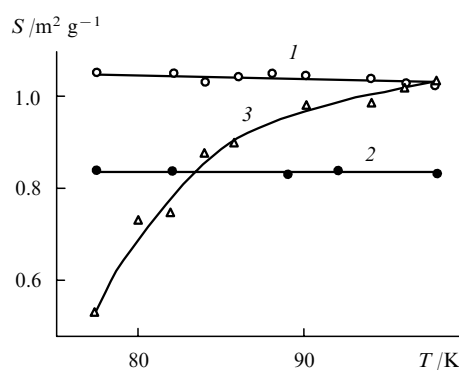


Figure 14. Temperature dependences of the specific surface measured by the BET technique from adsorption of Ar (1) and O_2 (2, 3) on the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ adsorbent in superconducting (1, 3) and non-superconducting states (2).²⁶³

A different situation is observed for the adsorption of paramagnetic oxygen molecules. At 77.4 K where the adsorbent is in the superconducting state, the amount of oxygen adsorbed in a monolayer is more than twice as small as that in the case of argon. As temperature increases, the amount of adsorbed oxygen increases, and when the adsorbent is no longer in the superconducting state, oxygen is adsorbed exactly in the same way as diamagnetic argon (see Fig. 14). Adsorption of oxygen on a non-superconducting adsorbent prepared by heating the original superconducting adsorbent in air to 873 K followed by quenching to room temperature was studied for reference purposes. In this case, the specific surface does not depend on temperature, and its small decrease in comparison with the specific surface of the original superconducting adsorbent is apparently due to partial sintering of small granules during thermal treatment of the ceramic at 873 K.

The anomaly observed in the low-temperature adsorption of molecular oxygen on HTSC ceramics is undoubtedly due to the

paramagnetism of O_2 molecules and the superconducting state of the adsorbent. It is believed²⁵⁹ that perfect diamagnetism of the adsorbent in the superconducting state favours its additional interaction with the paramagnetic oxygen molecule. However, estimates show that the energy of repulsion between the magnetic moment of oxygen and its mirror image in the superconducting adsorbent can be comparable with the energy of thermal movement only at distances equal to the molecular diameter. This does not consider the London penetration depth of magnetic field into the superconductor and the thickness of the possible non-superconducting phase layer on the adsorbent surface. A more reasonable assumption is that the repulsive force arises due to the interaction between the magnetic moment and the magnetic flux 'uptaken' by the granules of the superconducting adsorbent.²⁶⁷

As the temperature is increased, the adsorbent diamagnetism decreases and the amount of adsorbed oxygen increases synchronously, tending to a limit which corresponds to complete surface coverage. Measurements of the 'pure' heat of adsorption

$$Q_a = q_{st} - q_L,$$

(where q_{st} is the isosteric heat of adsorption and q_L is the heat of condensation of the adsorbate on a planar surface) also indicate a significant difference between the adsorption of molecular oxygen on superconducting and non-superconducting adsorbents. As the surface of a non-superconducting adsorbent is covered with oxygen, Q_a decreases monotonically (Fig. 15). This agrees with the common concept of adsorption on non-porous solids with the 'classical' non-uniform surface. Conversely, Q_a increases in the case of oxygen adsorption on superconducting adsorbents. This can be a consequence of the formation of new adsorption sites as the surface is covered with oxygen molecules due to violation of superconductivity in the near-surface zone by the strong magnetic field of the adsorbed molecules.

In continuation of previous works,^{263, 264} the heat transfer from a heater to a superconductor by argon, nitrogen, helium and oxygen molecules was studied.²⁶⁸ It is well known that the heat transfer from gas to solid occurs efficiently only in the case if the collision of the gas molecules with the surface is inelastic. Therefore, based on the above data on the adsorption of paramagnetic molecules,^{112, 263} it can be assumed that oxygen transfers heat to a superconductor less efficiently than molecules which have no magnetic moment. The efficiency of heat transfer by gas molecules to the surface of the $YBa_2Cu_3O_{7-x}$ superconducting ceramic was estimated as the time required for heating the specimen to T_c . Specimens of the $YBa_2Cu_3O_{7-x}$ ceramic had different critical parameters: the specimen Y1 was characterised by a large strength of the first critical magnetic field of the granules $H_{c1g} = 1.02 \times 10^4 \text{ A m}^{-1}$ and $T_c = 89.1 \text{ K}$, while the specimen Y2 had the following parameters: $H_{c1g} = 1.4 \times 10^3 \text{ A m}^{-1}$ and $T_c = 91.3 \text{ K}$. The electron micrographs of the cross-sections of specimens Y1 and Y2 taken with a scanning electron microscope showed that their morphologies differ essentially: the specimen Y1

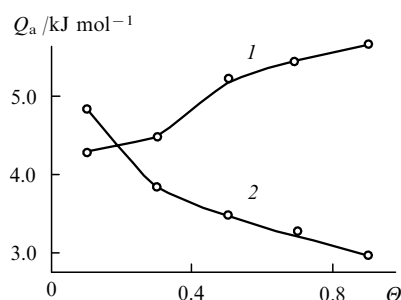


Figure 15. Dependence of the 'pure' heat of adsorption (Q_a) of oxygen on the $YBa_2Cu_3O_{7-x}$ ceramic in superconducting (1) and non-superconducting (2) state on the degree of surface coverage (θ) with molecular oxygen in the temperature range of 77.4–96 K.²⁶³

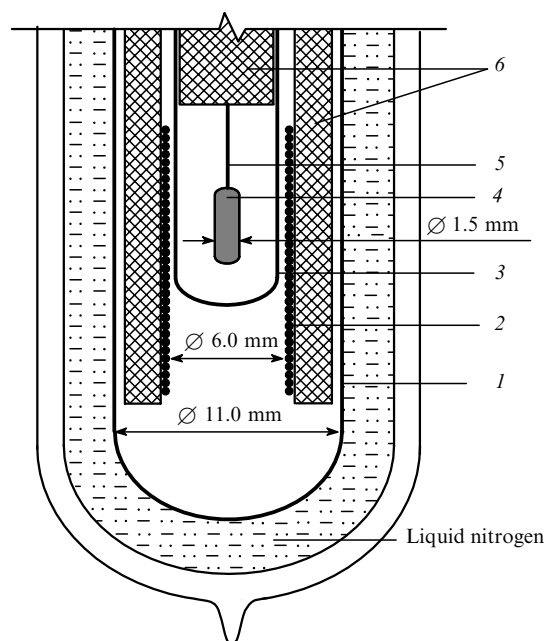


Figure 16. Scheme of measuring cell for recording the heating rate of HTSC materials in nitrogen or oxygen media;²⁶⁸ (1) external glass flask of the measuring cell; (2) heater; (3) quartz tube; (4) specimen; (5) capron thread; (6) thermal insulation.

consists of distinct oriented monolithic blocks with characteristic cross sizes of $\sim 40 \times 100 \mu\text{m}$, whereas the specimen Y2 consists of randomly oriented granules with an average size of $\sim 10 \mu\text{m}$.

The period from the moment when the heater has been turned on to the moment when the ceramic passes into the normal state was measured in different gaseous media in a cell (Fig. 16) placed in a mutual inductance coil for recording the magnetic susceptibility of the specimens. Figure 17 shows the experimental depend-

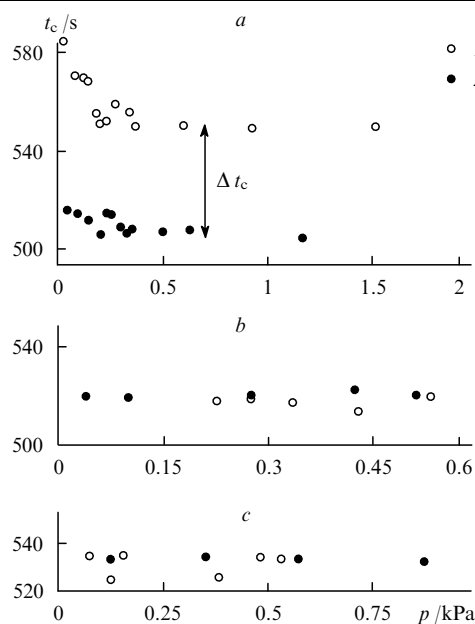


Figure 17. Dependence of the time required for heating a specimen to the superconducting transition temperature on the pressure of oxygen (1) and nitrogen (2) in the measuring cell;²⁶⁸ (a) measurements on the Y1 specimen; (b) measurements on the Y1 specimen coated with a paraffin film; (c) measurements on the Y2 specimen.

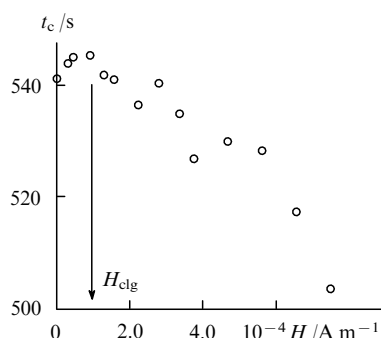


Figure 18. Dependence of the time of the Y1 specimen heating to the temperature of superconductivity loss on the external magnetic field strength.²⁶⁸

ences of time (t_c) required for heating the specimen to the superconducting transition temperature in a nitrogen or oxygen atmosphere on the pressure of these gases in the measuring cell. When the specimen Y1 was heated in oxygen, the time t_c was obviously greater than that in nitrogen. On the specimen Y2 and on the specimen Y1 coated with a paraffin film, the time t_c did not depend on the atmosphere in which heating was carried out. In addition, the time of heating of the specimen Y1 in oxygen depended on the strength of external magnetic field imposed on the specimen after cooling (Fig. 18). The time t_c remained unchanged if the strength of the external magnetic field did not exceed H_{clg} for the particular specimen. Further increase in field strength resulted in a decrease in t_c . Based on these experiments, it can be concluded that heat transfer by oxygen molecules to a superconducting specimen with high critical parameters occurs with lower efficiency.

The essential difference of the oxygen molecule from the nitrogen molecule is its magnetic moment, therefore it can be believed that its interaction with the superconductor is responsible for the observed phenomenon. As shown above,²⁶³ the magnetic moment of oxygen can favour the decrease in its adsorption on the superconductor surface. Apparently, in this case the oxygen molecules transfer heat less efficiently because they are elastically reflected from the superconductor surface. Taking into account that the character of collisions of oxygen molecules with a superconductor surface depends on its critical parameters, it is possible to suggest a new model of the interaction of the magnetic moment of oxygen with superconductors. In contrast to the previously suggested model of interaction between the magnetic moment and the Meissner superconductor phase,²⁵⁹ it is assumed^{267,269} that the repulsive force of the magnetic moment from the superconductor surface is described by the power function

$$F \propto d^{-n},$$

where the index n depends on the distance d between the magnet creating the magnetic field and the superconductor. At long distances and in the cases where the magnetic field strength of the magnet does not exceed the first critical field strength of the superconductor, $n = 4$; this corresponds to the ordinary dipole–dipole interaction. At short distances, *i.e.*, in sufficiently strong magnetic fields, the character of interaction of the magnet with the superconductor changes substantially. The magnetic field of the magnet penetrates into the superconductor bulk; as a result, the superconductor passes into a mixed state. In this case, interaction is described by the vortical model, according to which the magnetic flux from the magnet is ‘uptaken’ by the bulk of the granules, creating a grid of vortical lines reaching the superconductor surface and capable of interacting with the magnet. The interaction energy is expressed by the formula²⁷⁰

$$E = \frac{mH_{clg}\delta}{\pi d}, \quad (5)$$

where m is the magnetic moment and δ is the superconductor thickness. It should be noted that in this case the energy of interaction depends on distance much more weakly than in the Meissner model (d^{-1} instead of d^{-3}).

According to the estimate made, the energy of interaction between the magnetic moment of oxygen and the surface of the specimen Y1 is rather high and is comparable with the thermal energy kT at a distance $d \approx 5$ nm. This distance is much larger than the oxygen molecule size and the thickness of the possible non-superconducting phases usually present on HTSC surfaces. The energy of interaction with the surface of the specimen Y2 becomes equal to the thermal energy kT only at $d \approx 0.05$ nm, which is less than the oxygen molecule size, hence repulsion does not occur in this case. This agrees with the experimental results mentioned above.

Thus, superconductivity affects the adsorption and collision of paramagnetic molecules with the superconductor surface.^{263,264,268} It is important that these processes are also controlled by the external magnetic field.²⁷¹

Heterogeneous chemical reactions are very ‘sensitive’ to the state of the surface. The recoil force, which appears during desorption of hydrogen molecules which acquire nonequilibrium translational energy upon their recombination at the surface was measured after keeping a $YBa_2Cu_3O_{7-x}$ superconductor in a stream of hydrogen atoms.²⁷² The measurements were carried out by the weighing method in the temperature range of 78–350 K. The recoil force did not depend on temperature as long as the superconductor was in the ordinary state. After its transition to the superconducting state, a decrease in the recoil force was recorded. This was explained by a change in the magnetic state of the surface. The temperature dependence of the recoil force correlates well with changes in the relative intensity of the ferromagnetic resonance absorption of the superconductor. This correlation suggests that the recombination of hydrogen atoms occurs at the antiferromagnetically ordered Cu^+ surface ions. Cooling of the substrate changes the magnetic ordering and hence affects the concentration of the Cu^+ ions at the surface. The decrease in the recoil force below the superconducting transition temperature of the substrate is apparently due to magnetic shielding of the Cu^+ ions due to of the total diamagnetism of the superconductor.

The low-temperature catalytic reaction of the *ortho*–*para* conversion of molecular hydrogen on the superconducting catalyst $YBa_2Cu_3O_{7-x}$ was studied.^{273,274} The catalytic activity of the superconductor at various temperatures was estimated by chromatographic measurement of the amplitude of *para*-hydrogen signal on exit from the reactor. The temperature dependence of the effective rate constant of catalytic *ortho*–*para* conversion is

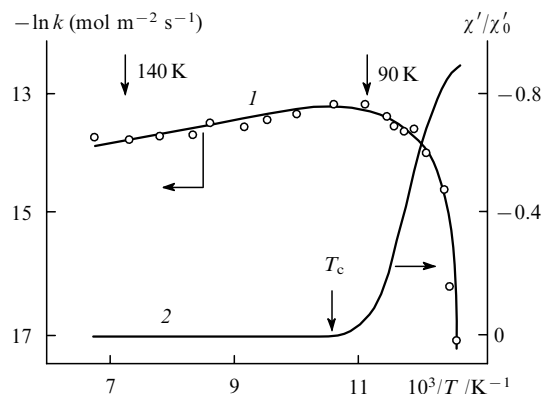


Figure 19. Temperature dependences of the effective rate constant of the *ortho*–*para* hydrogen conversion on the superconducting catalyst $YBa_2Cu_3O_{7-x}$ (1) and the real part of the relative magnetic susceptibility of this catalyst (2).²⁷³

presented in Fig. 19. One can see that the conversion rate decreases abruptly starting from 90 K. This temperature is close to the superconducting transition temperature of the catalyst determined from magnetic susceptibility (see Fig. 19, curve 2). Analysis of the possible magnetic mechanisms of hydrogen *ortho*–*para* conversion on oxide catalysts^{275–278} made it possible to conclude that the magnetic state of the catalyst's surface plays an important role in these processes. Before a catalyst is transferred to the superconducting state, *ortho*–*para* conversion of hydrogen occurs on the paramagnetic centres; the Cu²⁺ cations play this role in HTSC materials. Superconductivity changes essentially the magnetic state of the catalyst and it acquires a new property, *i.e.*, becomes a pure diamagnetic. The currents flowing along the surface shield the magnetic field of the paramagnetic centres and thus 'switch off' the basic mechanism of the low-temperature catalytic *ortho*–*para* conversion. As a result, the effective reaction rate constant decreases by several orders of magnitude.

VI. Conclusion

Analysis of the experimental and theoretical data presented above shows that the specific features of interaction of external molecules with HTSC materials are determined by a wide range of various physicochemical processes. The thermodynamic metastability of almost all of the known high-temperature superconductors^{60, 279, 280} probably has certain impact on the processes involved in the synthesis of HTSC materials and on the effects of external molecules on these processes. The study of superconductivity in HTSC materials requires rather complex problems to be solved. Of these, the reproducible synthesis and chemical stability of the final material present important problems. Apparently, the wide scatter of the experimental results for the thermodynamic characteristics, critical parameters of superconductivity, *etc.* reported by different authors is due to this problem. Nevertheless, a number of important conclusions can be made.

1. Depending on the temperature of treatment of oxide HTSC materials by foreign molecules of simple compounds, the phenomena resulting from their effect on the superconductivity of these materials can be separated in two groups.

The phenomena observed on treatment of HTSC materials at temperatures up to 473 K correspond to the first group. As a rule, such treatment little affects superconductivity. It is important that this problem is far from clarified even now, despite numerous publications on this matter. The experimental results obtained by different groups of authors and the conclusions made on this basis on the nature of the effect are usually contradictory and inconsistent. Nevertheless, studies in this temperature range are very important for understanding the physicochemical processes that occur on superconductor surfaces.

The second group includes phenomena caused by treatment of HTSC materials at temperatures above 473 K. Such treatment often affects strongly the parameters of superconductors. As a rule, the experimental results obtained in different studies are reproduced satisfactorily. The effect of simple molecules on the properties of superconductors in this temperature range is caused by the intercalation of molecules in its crystal lattice and/or by their chemical reactions with the ions of an HTSC material. As a rule, the action of simple molecules at temperatures above 473 K results in superconductivity degradation.

Intercalation of oxygen, which plays a key role in the formation of the superconducting phase, deserves special attention. Numerous studies showed that halogen molecules or atoms incorporated in the lattices of HTSC ceramics can play the same role as the oxygen atoms. For example, the non-superconducting tetragonal phase of YBa₂Cu₃O_{7–x} passes in the superconducting orthorhombic phase upon intercalation of halogens.

2. The range of effects of organic compounds on the characteristics of superconductivity is much more diverse. The first studies

along this line carried out on low-temperature superconductors showed that the donor–acceptor interaction of organic molecules with the superconductor material results in a considerable change in the critical parameters of superconductivity. The changes in T_c and I_c correlate with the electronegativity of the adsorbed molecules. Similar phenomena were observed later in the studies of HTSC materials.

The superconductivity parameters of oxide materials depend on the electronic properties of adsorbed molecules or a deposited polymeric film. Dielectric polymers little affect superconductivity, whereas conducting polymers decrease T_c . This effect is apparently due to the 'proximity' effect.

It has been proven that intercalation of planar organic molecules into the space between the crystal lattice layers in HTSC materials changes their characteristics considerably. In some cases the specimens display unusual physical properties.

Adsorption of stable organic radicals affects the magnetic state of the superconductor surface and the electric resistance of the intergranular layers; as a result, I_c changes.

3. In turn, superconductivity can affect noticeably various physicochemical processes occurring on the superconductor surface. For example, transition of a material into the superconducting state changes the luminescence characteristics of organic dyes adsorbed on the surface of an HTSC material (the quantum yield and the position of the maximum in the luminescence spectrum). Systems in which the energy of interaction between the superconductor and paramagnetic molecules from the environment is comparable with the energy of the adsorption interaction were found among HTSC materials. Owing to this, superconducting membranes can separate gas mixtures of paramagnetic and diamagnetic molecules. At the liquid nitrogen temperature, the superconducting adsorbent adsorbs paramagnetic oxygen molecules several-fold more weakly than diamagnetic argon atoms. This is probably due to the repulsive interaction of the magnetic moment of the molecule with the magnetic flux 'uptaken' by the specimen granules.

4. The low-temperature heterogeneous-catalytic *ortho*–*para* hydrogen conversion occurring at the paramagnetic centres of the adsorbent is also very sensitive to the surface state, and its rate decreases by several orders of magnitude as the catalyst passes into the superconducting state. This phenomenon can be explained by shielding of the catalytically active paramagnetic centres located on the superconductor surface, which is caused by the substrate diamagnetism.

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The synthesis of porphyrins from dipyrrolylmethanes

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Abstract. The methods for the synthesis of pyrroles, dipyrrolylmethanes and porphyrins derived from them are analysed, systematised and generalised. The bibliography includes 82 references.

I. Introduction

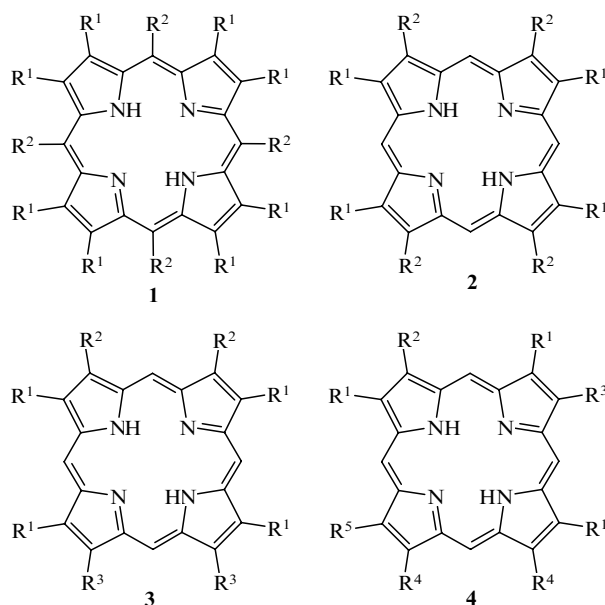
The methods for the synthesis of porphyrins are highly diverse and their choice is determined by the nature and mutual arrangement of substituents to be incorporated into the porphyrin molecule. Those suitable for the preparation of relatively simple porphyrins can be inapplicable for the synthesis of more complex compounds. Consideration of these methods is appropriate to begin with a brief survey of different types of porphyrins (compounds **1–4**).

The first type of porphyrins includes those which comprise identical substituents in the β -positions of the pyrrole rings and symmetrical *meso*-substituted porphyrins (compounds **1**). These compounds are usually prepared by one-step condensation of four identical pyrrole molecules into porphyrin.

The second type of porphyrins (porphyrins **2**) have a more complex structure which retains certain features of symmetry. These compounds are synthesised *via* intermediate dipyrrolylmethanes, -methenes and pyrroketones; since these molecules contain two different substituents, four isomeric products can be formed.

The third group of porphyrins includes porphyrins **3** with three different substituents and symmetrical dipyrrolic fragments. In some cases, dipyrroles can be used as precursors of porphyrins **3**.

The fourth type of porphyrins (porphyrins **4**) comprise more than three different substituents. Their synthesis is preceded by the formation of linear tetrapyrrole molecules which are closed to form the corresponding cyclic structures in the final stage. Thus, *a*- and *b*-oxobilanes, *b*-bilenes and *a,c*-biladienes are typically used as intermediate compounds.



To date, numerous novel procedures for the synthesis of porphyrins have been developed. However, all of them include the formation of methine bridges from methyl or bromomethyl groups in the α -position of pyrrole, dipyrrolylmethane or -methene. The choice of a synthetic procedure is largely determined by the desired symmetry of the porphyrin molecule. The syntheses based on the use of symmetrical dipyrrolylmethanes the cyclisation of which yields porphyrins with a high degree of symmetry (C_{2v}) are of particular interest in this respect. The obvious advantages of this method are the simplicity of preparation of starting dipyrrolylmethanes and sufficiently high yields (50%–60%) of porphyrins. Bisdipyrrolylmethanes were used in the synthesis of sterically hindered, dimeric and polymeric porphyrins.

II. Synthesis of pyrroles

Pyrroles are the key compounds in the synthetic chemistry of porphyrins. These compounds are readily available and yield porphyrins upon condensation. This circumstance determined the wide application of pyrroles in the synthesis of *meso*-alkyl- and *meso*-arylporphyrins including a whole array of sterically hindered porphyrins.

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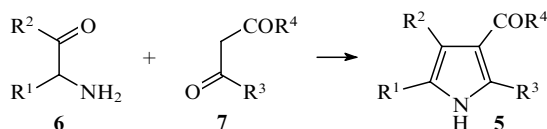
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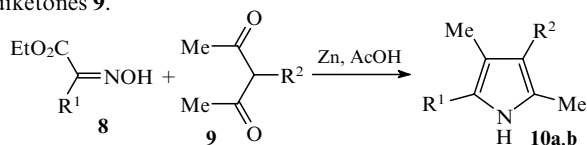
Unsubstituted pyrrole is usually prepared by pyrolysis of ammonium mucate.¹ Substituted porphyrins can be synthesised in two ways, *viz.*, by chemical modification of the macrocycle and by condensation of pyrroles with a predetermined set of substituents. The latter approach is more advantageous, since it provides greater scope for synthesis.

A vast variety of pyrroles have been described in the literature. The derivatives **5** containing electron-withdrawing groups are synthesised, as a rule, by the Knorr method,² *viz.*, by condensation of aminoketones **6** with β -dicarbonyl compounds **7**.



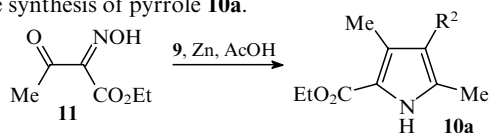
The aminoketones **6** are usually prepared by the reduction of the oximes which, in turn, are formed upon nitrosation of ketones or β -dicarbonyl compounds with sodium nitrite in glacial acetic acid.² Zinc in acetic acid is typically used as the reducing agent. Although the yields in this synthesis do not exceed 40%–60%, this procedure has found wide application owing to simplicity and availability of the starting compounds.

Kleinspehn³ performed the synthesis of α -ethoxycarbonyl (**10a**) or α -cyanopyrroles **10b** by condensation of oximes **8** with β -diketones **9**.

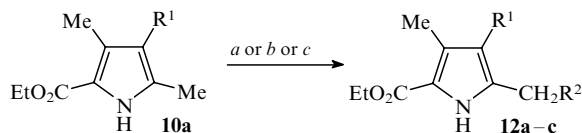


R¹ = CO₂Et (**a**), CN (**b**).

Later, it was shown⁴ that α -hydroxyimino β -keto esters, *e.g.*, compound **11**, can also enter into the reaction of reductive condensation with alkyl- β -diketones. This method was used in the synthesis of pyrrole **10a**.



Pyrroles containing a halogenomethyl or an acetoxymethyl group in one of the α -positions are most commonly used in the synthesis of dipyrrolylmethanes. Different approaches to the synthesis of these compounds were compared by Semeikin *et al.*⁵ α -Chloromethylpyrroles **12a** are prepared by treatment of pyrroles **10a** with sulfuryl chloride or *tert*-butyl hypochlorite on cooling.⁵ The yields of reaction products strongly depend on the temperature of the reaction mixture. Diethyl ether, dichloromethane or glacial acetic acid are used as the solvents. Bromination of α -methylpyrroles **10a** with molecular bromine in diethyl ether or acetic acid results in strong resinification which significantly reduces the yields of pyrroles **12b**.

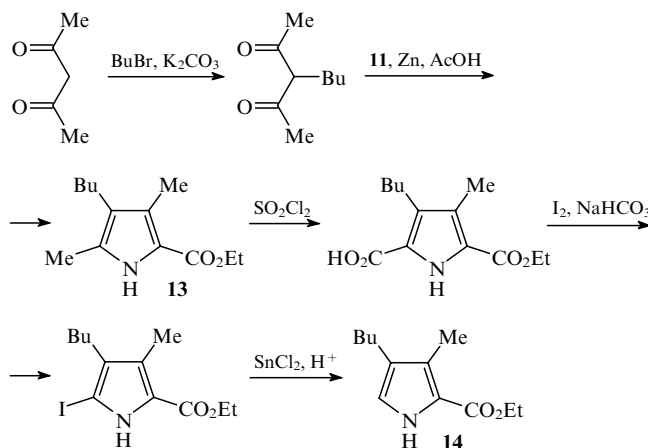


(a) SO₂Cl₂ [**12a**, R² = Cl (85%)]; (b) Br₂ [**12b**, R² = Br (73%)];

(c) Pb(OAc)₄ [**12c**, R² = OAc (95%)].

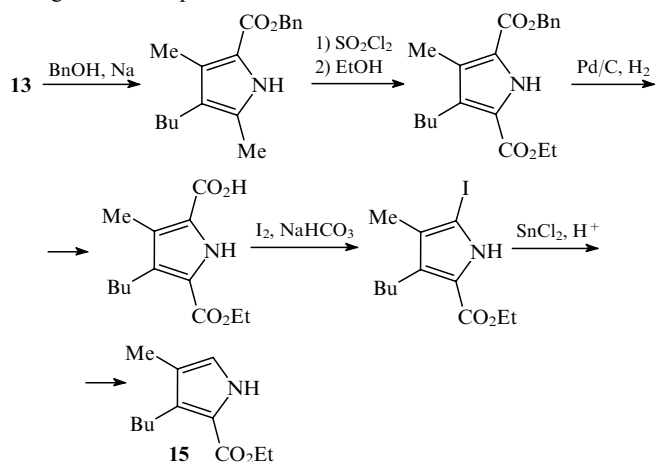
Acetoxymethylpyrroles **12c** can be prepared by the reaction of the halogenomethyl derivatives **12a,b** with sodium acetate in acetic acid; however, direct oxidation of α -methylpyrroles **10a** with lead tetraacetate is more efficient.⁵ Acetoxymethyl derivatives are less readily hydrolysed and oxidised in air than compounds **12a,b**, which makes them especially attractive for further syntheses.

The methods for the synthesis of isomeric butylpyrrole derivatives in high yields have been proposed.^{6–10} The reaction of acetylacetone with butyl bromide in DMF or acetone in the presence of anhydrous potassium carbonate yields 3-butylpentane-2,4-dione; its condensation with ethyl hydroxyiminoacetate **11** in the presence of acetic acid and zinc dust gives 4-butyl-2-ethoxycarbonyl-3,5-dimethylpyrrole (**13**).



As a rule, α -monosubstituted pyrroles are the target products in such syntheses. The oxidation of the α -methyl group of pyrrole **13** with sulfuryl chloride in diethyl ether results in 4-butyl-5-carboxy-2-ethoxycarbonyl-3-methylpyrrole. Its decarboxylation is carried out in two steps, *viz.*, by substitution of iodine for the carboxy group by treatment with iodine and sodium hydrogen carbonate in aqueous ethanol and subsequent reduction of the α -iodopyrrole formed with tin dichloride. These reactions result in 4-butyl-2-ethoxycarbonyl-3-methylpyrrole (**14**) in sufficiently high yield.^{6–10}

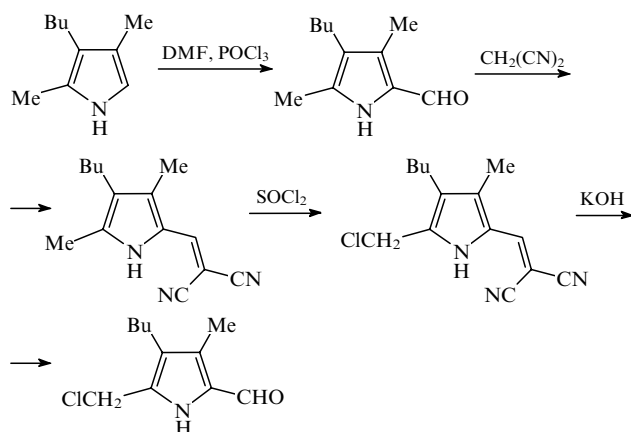
A reaction sequence was proposed^{6–10} which leads to 3-butyl-2-ethoxycarbonyl-4-methylpyrrole (**15**), a key compound in the synthesis of many di- and tetrapyrroles,[†] from the readily available α -ethoxycarbonylpyrrole **13**. To this end, compound **13** was transesterified with benzyl alcohol; the resulting ester was oxidised with sulfuryl chloride at the α -methyl group and esterified with ethanol. The diester formed was subjected to hydrogenolysis on a palladium catalyst. The resulting 3-butyl-5-carboxy-2-ethoxycarbonyl-4-methylpyrrole was decarboxylated *via* the iodo derivative using a standard procedure:



The pyrroles **14** and **15** can be used for further transformations both directly and in the form of formyl derivatives which can be

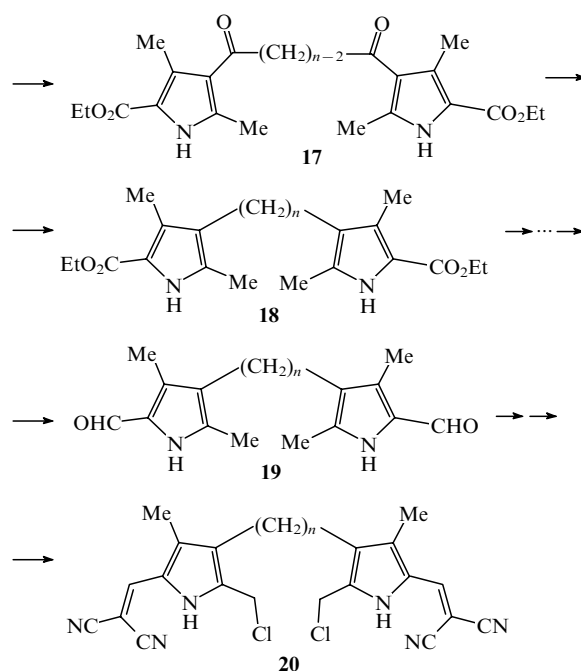
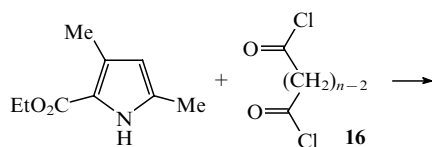
[†] It is of note that only α -unsubstituted pyrroles containing a small methyl group in the vicinal β -position have previously been used in the synthesis of dipyrrolylmethanes.^{11–20} However, later it was found that the steric factor has no effect on the condensation reaction.^{7, 21–23}

easily obtained by the reaction of these pyrroles with dimethylformamide in the presence of phosphorus oxychloride or benzoyl chloride. In many reactions, *e.g.*, in chlorination with thionyl chloride, the aldehyde group is protected.^{7,24} To this end, formylpyrroles are treated with dicyanomethane; deprotection is carried out by alkaline treatment. This procedure was used in the synthesis of 4-butyl-5-chloromethyl-3-methylpyrrole 2-carbaldehyde from 3-butyl-2,4-dimethylpyrrole.



Dipyrrole structures in which pyrrole rings are linked through β -positions can be prepared from more readily available β -unsubstituted pyrroles.^{25–27} These structures and the possibilities of their chemical modification present special interest, since they permit the design of novel types of porphyrin molecules.

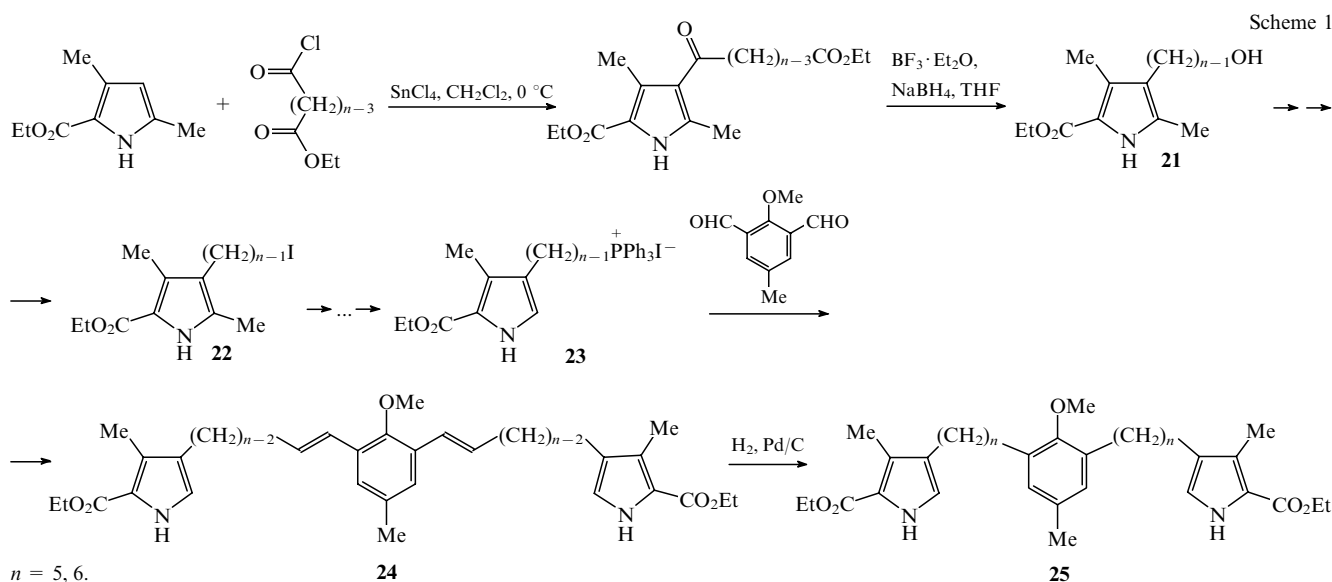
The acylation of 3,5-dimethyl-2-ethoxycarbonylpyrrole with the dicarboxylic acid chloride **16** and subsequent reduction of the carbonyl groups of the diketone **17** formed with diborane result in compound **18**. The bispyrrole **18** is further converted into the benzyl ester, which is further subjected to hydrogenolysis followed by decarboxylation and formylation, eventually resulting in the aldehyde **19**.²⁵ The formyl groups of the dialdehyde are protected with dicyanomethane as described above, which is followed by chlorination with sulfur chloride. This method was used in the synthesis of the dipyrrole derivatives **20**.²⁵



$n = 9-11$.

Later, Morgan and Dolphin²⁷ synthesised β -linked dipyrrolic derivatives containing an aryl fragment in their bridges. The acylation of 3,5-dimethyl-2-ethoxycarbonylpyrrole and subsequent reduction of the carbonyl group result in the hydroxy derivative **21**, which is converted into the iodo derivative **22** on substitution of iodine for the hydroxy group *via* the corresponding mesylate. The methyl group in compound **22** is eliminated from position 5 using the standard procedure, *i.e.*, *via* 5-iodopyrrole. Subsequent reaction with triphenylphosphine in boiling toluene affords the phosphonium salt **23**. Its condensation with 2,6-diformyl-4-methylanisole in dioxane in the presence of potassium carbonate results in the diene **24**. The final step in this synthesis is the catalytic hydrogenation of compound **24** leading to the target dipyrrole derivative **25** (Scheme 1).

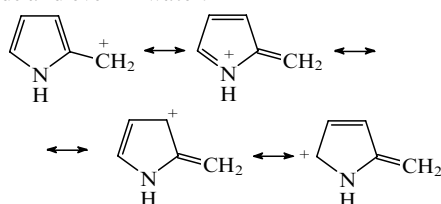
Syntheses based on β -unsubstituted pyrroles are multistage processes, which is the common drawback, chemical conversions involve alternately α - and β -positions of the ring, which significantly complicates the synthesis. In our opinion, the use of relatively available α -unsubstituted pyrroles is more advantageous.



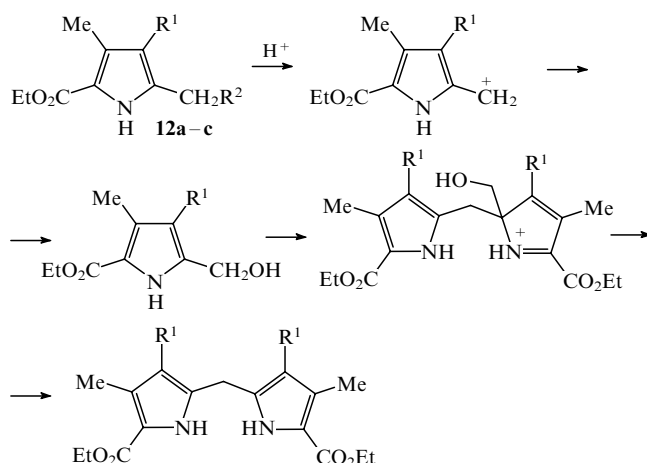
III. Synthesis of dipyrrolylmethanes

Porphyrins can also be synthesised from dipyrrolylmethanes and -methenes. However, both of them possess exceedingly high reactivity. This disadvantage can be overcome through the introduction of electron-withdrawing substituents. Synthesis of dipyrrolylmethanes containing such substituents is problematic. On the other hand, there exist simple and efficient procedures for the synthesis of stabilised dipyrrolylmethanes; their advantages in the synthesis of structurally complex porphyrins leave no doubt.^{28,29}

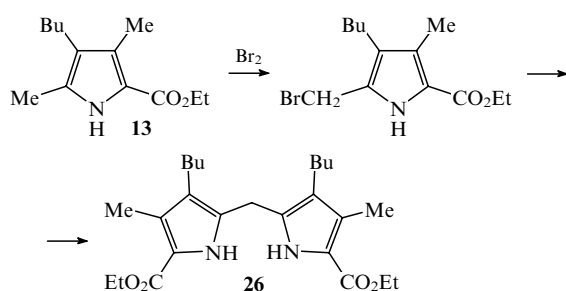
It has been established that the condensation of pyrroles **12a–c** occurs *via* pyrrolylmethyl carbocations stabilised due to the delocalisation of the positive charge.² Such cations are relatively stable both in inert solvents and in alcohols, carboxylic acids and even in water.



On boiling in ethanol in the presence of hydrobromic acid, pyrroles **12a–c** are converted into dipyrrolylmethanes in high yields.^{2,5,7,30,31} If such pyrroles contain alkyl substituents in the β -positions, dipyrrole compounds are obtained in up to 90% yields.

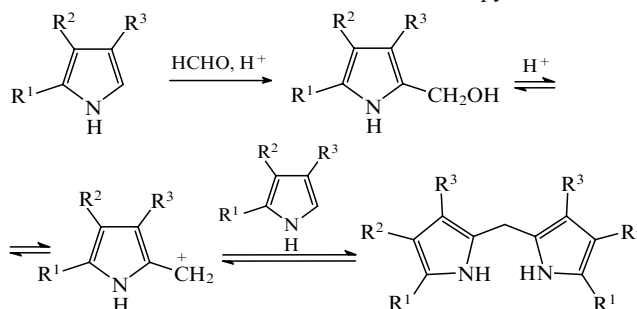


An efficient procedure for the synthesis of dipyrrolylmethanes containing butyl groups in positions 3 and 3' has been proposed.^{7–10,24,29,32} Bromination of the α -methyl group of the pyrrole **13** with subsequent condensation of 5-bromomethyl-4-butyl-2-ethoxycarbonyl-3-methylpyrrole in ethanol in the presence of an acid results in the 5,5'-diethoxycarbonyl derivative **26**; its alkaline hydrolysis affords bis(3-butyl-5-carboxy-4-methylpyrrol-2-yl)methane. As in the case of synthesis of bis(5-carboxy-3,4-dimethylpyrrol-2-yl)methane, lead tetraacetate proved to be the best oxidant for the starting pyrrole.⁵

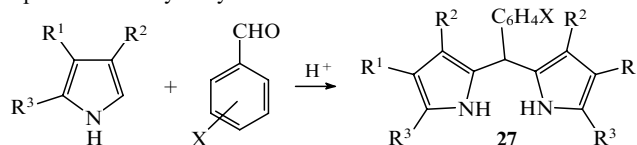


Symmetrical dipyrrolylmethanes can also be prepared by the condensation of α -monosubstituted pyrroles with aldehydes. It is

self-evident that the β -positions of the pyrrole ring must be substituted with at least one electron-withdrawing substituent, which thus stabilises the product.³³ This reaction occurs under the same conditions as the self-condensation of the pyrroles **12a–c**.



The reaction of 2-benzyloxycarbonyl-3,4-dimethylpyrrole with benzaldehyde in ethanol in the presence of hydrochloric acid results in *meso*-phenyldipyrrolylmethane **27a**. Under conditions of acid catalysis, 3-butyl-2-ethoxycarbonyl-4-methylpyrrole (**15**) reacts with benzaldehyde to give dipyrrolylmethane **27b**.⁸ It was shown^{7,23} that the reaction of 4-butyl-2-ethoxycarbonyl-3-methylpyrrole (**14**) with benzaldehyde and its derivatives (XC₆H₄CHO, X = OMe, NO₂, NMe₂) in the ethanol–hydrochloric acid system results in *meso*-aryl-substituted dipyrrolylmethanes **27c–i** in good yields. Similar to compounds **27a,b**, these products (except for compound **27i** which undergoes resinification) are converted into the corresponding dicarboxy derivatives upon alkaline hydrolysis.



Compound 27	R ¹	R ²	R ³	X
a	Me	Me	CO ₂ Bz	H
b	Bu	Me	CO ₂ Et	H
c	Me	Bu	CO ₂ Et	H
d	Me	Bu	CO ₂ Et	4-OMe
e	Me	Bu	CO ₂ Et	3-OMe
f	Me	Bu	CO ₂ Et	2-OMe
g	Me	Bu	CO ₂ Et	4-NO ₂
h	Me	Bu	CO ₂ Et	3-NO ₂
i	Me	Bu	CO ₂ Et	3-NMe ₂

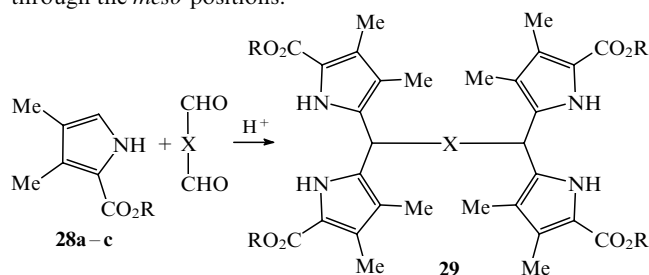
The structures of a series of *meso*-substituted dipyrrolylmethanes were calculated by the molecular mechanics methods (the force field MM⁺).^{34–36} The strain energies of isomeric compounds of the type **27** are listed in Table 1.

Table 1. The strain energies of isomeric dipyrrolylmethanes **27** (E_{MM} /kJ mol^{−1}) and their constituents, *viz.*, bond strain energies (E_{bnd}), bond angle energies (E_{ang}), torsion angle energies (E_{dih}) and Van der Waals energies (E_{vdw}).

R ¹	R ²	R ³	Y ^a	E_{MM}	E_{bnd}	E_{ang}	E_{dih}	E_{vdw}
H	H	H	H	97	3.66	86.1	−12.0	−7.0
Me	Bu	CO ₂ Et	H	139	2.28	133.5	−12.8	16.8
Me	Bu	CO ₂ H	H	111	1.49	93.4	−6.0	2.3
Bu	Me	CO ₂ Et	Ph	106	3.20	100.3	−31.7	20.2
Me	Bu	CO ₂ Et	Ph	104	2.83	92.3	−28.1	10.2
Me	Et	CO ₂ Et	Ph	105	2.56	87.5	−24.2	10.1
Bu	Me	CO ₂ H	Ph	86	0.73	67.8	−17.7	8.0
Me	Bu	CO ₂ H	Ph	83	1.49	75.6	−21.4	4.3
Me	Et	CO ₂ H	Ph	87	1.78	72.4	−16.2	4.1

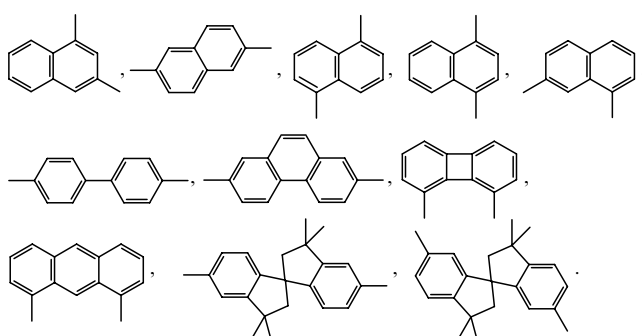
^a Y is *meso*-substituent.

The above-described procedure is widely employed in the synthesis of bisdipyrrolylmethanes.^{13–16, 18, 22} The reaction of pyrroles **28a–c** with dialdehydes in acid media gives high yields of compounds **29** the dipyrrolic fragments of which are linked through the *meso*-positions.



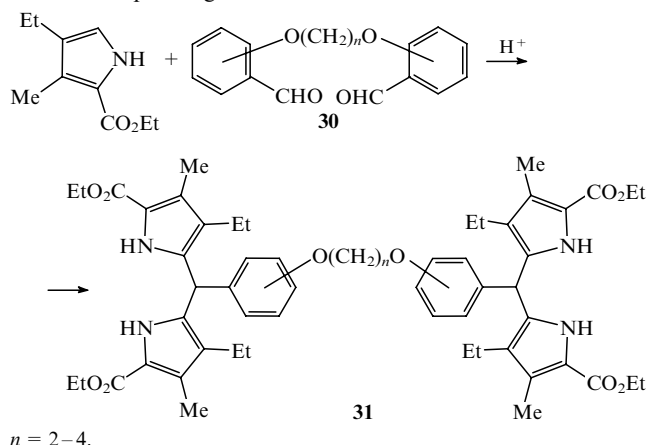
R = H (**a**), Et (**b**), Bn (**c**);

X = (CH₂)_n (n = 4, 6, 12), , , ,



3-Methyl-2-ethoxycarbonyl-4-ethylpyrroles are easily condensed in acid media with dialdehydes **30** the phenyl fragments

of which are linked by ether bridges [O(CH₂)_nO] of different lengths (n = 2–4).²³ The resulting esters **31** are easily hydrolysed to the corresponding acids in alkaline media.



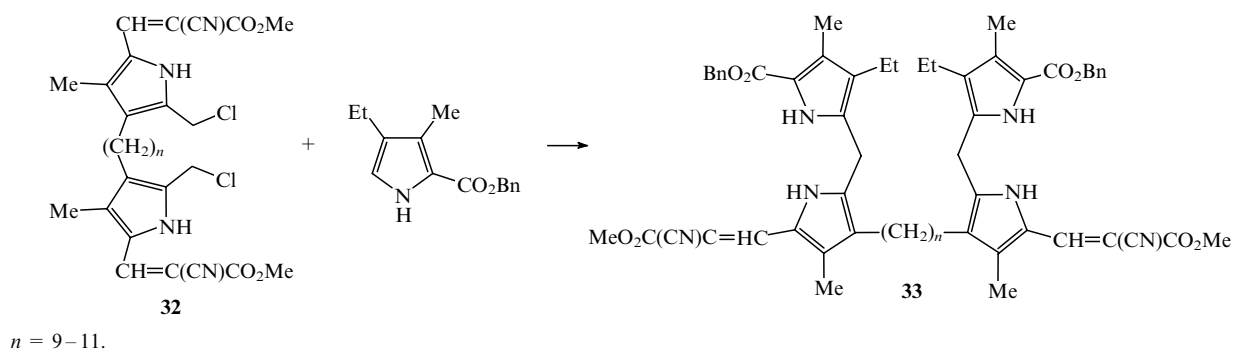
n = 2–4.

Compounds with fundamentally different structures can be prepared on the basis of β -linked pyrroles. The condensation of bispyrroles **32** containing chloromethyl groups with 2-benzyloxycarbonyl-4-ethyl-3-methylpyrrole in acetic acid results in bisdipyrrolylmethanes **33** the dipyrrolic fragments of which are linked by methylene bridges through the 3,3'-positions (n = 9–11) (Scheme 2).²⁵

An alternative approach involves the condensation of 5,5'-unsubstituted bispyrrole **34** with the α -chloromethyl derivative **35** (Scheme 3).²⁷

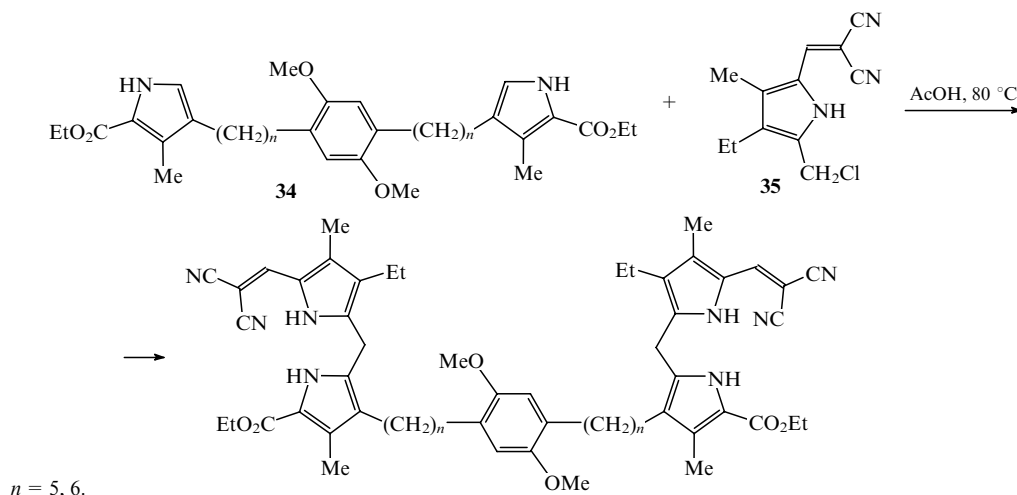
The reaction of compounds of the type **12a–c** with α -unsubstituted pyrroles gives nonsymmetrical dipyrrolylmethanes. It was proposed³⁷ to start from bromomethylpyrrole in a sodium acetate–glacial acetic acid buffer. It is the intermediate acetoxy-methylpyrrole formed that enters into the reaction. Unfortu-

Scheme 2



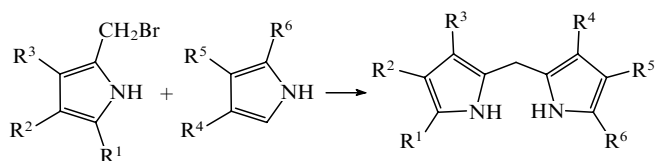
n = 9–11.

Scheme 3

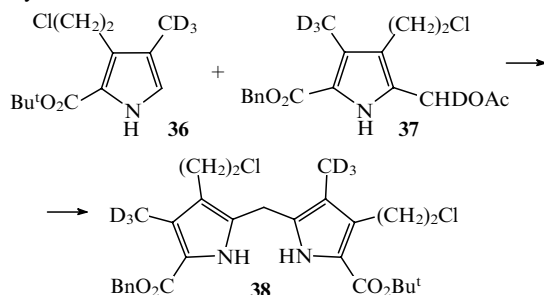


n = 5, 6.

nately, this reaction yields a large amount of the symmetrical dipyrrolylmethane as the side product.



The reaction of pyrroles **36** and **37** in the presence of *p*-toluenesulfonic acid in AcOH gives dipyrrolylmethane **38** in 85% yield.³⁸

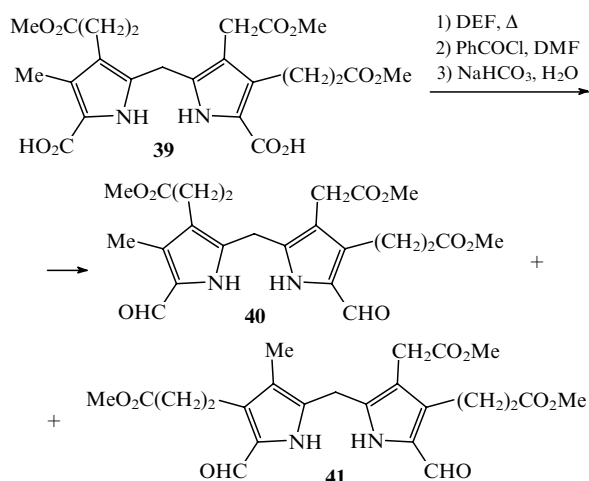


Other methods for the synthesis of dipyrrolylmethanes are less popular. If chemical modification of dipyrrolylmethanes is envisaged, allowance must be made for the fact that their stabilities and reactivities with respect to electrophilic reagents are similar to those of pyrroles. Dipyrrolylmethanes are stable if they contain at least one electron-accepting group in each of their pyrrole nuclei. Also the methylene unit in dipyrrolylmethanes is readily oxidised to form dipyrrolylmethenes or ketone.

Dipyrrolylmethane 5,5'-dicarboxylic acids are prepared by heating the corresponding 5,5'-diethyl esters with aqueous alkalis with subsequent precipitation of the reaction product with a mineral acid or by hydrogenation of 5,5'-dibenzyl esters on a palladium catalyst in THF at atmospheric pressure and at room temperature.^{7, 32}

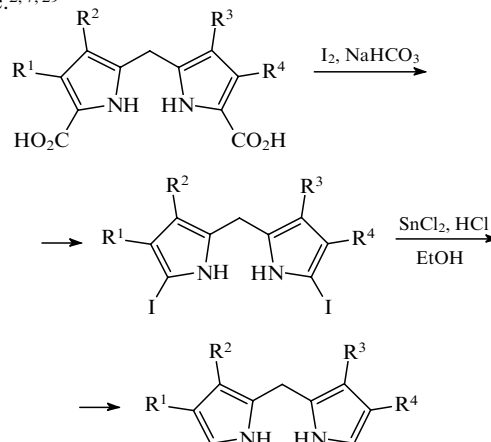
Heating of dry bis(5-carboxypyrrol-2-yl)methanes is accompanied by profound destruction; therefore, McDonald *et al.*³⁹ proposed to conduct the decarboxylation in sealed tubes in aqueous solutions of alkalis at 170–180 °C, which causes only partial destruction. In an alternative procedure,⁴⁰ the decarboxylation is carried out by boiling the dicarboxylic acids prepared from diethyl esters in DMF in an inert atmosphere.

N,N-Diethylformamide was used as a solvent for increasing the boiling temperature of the reaction mixture.⁴¹ Unfortunately, the decarboxylation of dipyrrolylmethane **39** is accompanied by intramolecular rearrangements. Subsequent formylation gives a mixture of dialdehydes **40** and **41** in a total yield of 60%.

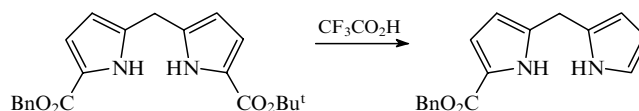


DEF is *N,N*-diethylformamide.

If dipyrrolylmethanes have different substituents in the β-positions of the pyrrole ring, a mixture of isomeric products can be formed. To avoid this, the decarboxylation is carried out in two steps. First, the carboxy groups are substituted by iodine and then the iodo derivatives are reduced, *e.g.*, with tin(II) chloride.^{2, 7, 29}

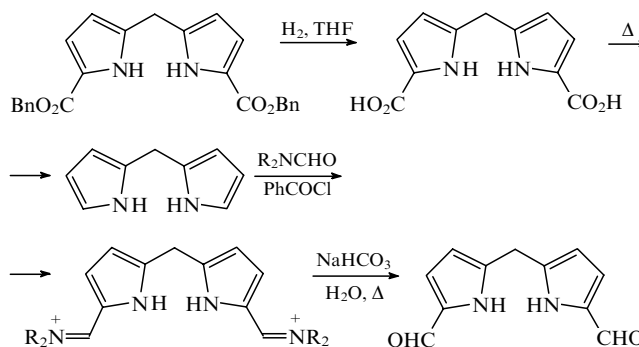


Dipyrrolylmethane dicarboxylic acids can be decarboxylated by trifluoroacetic acid (TFA). It was found⁴² that 5,5'-unsubstituted dipyrrolylmethanes thus formed are stable in TFA at room temperature for a week. Trifluoroacetic acid was used, for example, for decarboxylation of 5-benzoyloxycarbonylpyrrol-2-yl-5'-*tert*-butoxycarbonylpyrrol-2'-ylmethane.⁴² However, TFA can induce intramolecular rearrangements in dipyrrolylmethanes.



Heating of carboxy derivatives in aqueous alkalis in the presence of hydrazine as a stabiliser seems to be the method of choice for decarboxylation of β-alkylated dipyrrolylmethanes.^{8, 29} In this case, the yield of the target product reaches 85%.

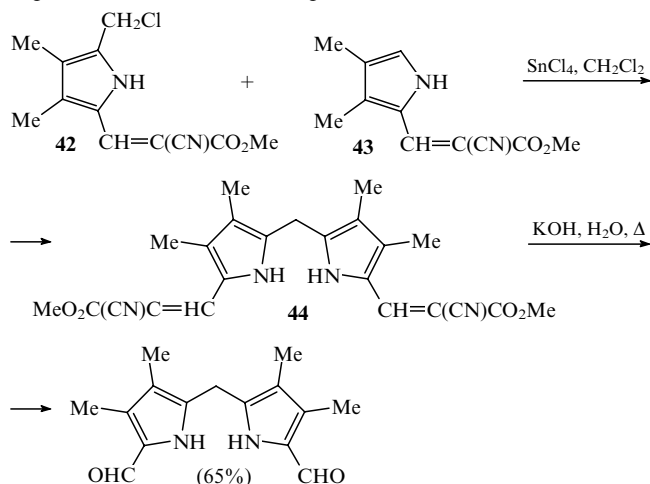
Bis(5-formylpyrrol-2-yl)methane was obtained from bis(5-benzoyloxycarbonylpyrrol-2-yl)methane by the Wilsmeier reaction. The use of phosphorus oxychloride or benzoyl chloride results in dialdehydes with practically equal yields (45%–50%).³³



An alternative procedure for the synthesis of dipyrrolylmethanedialdehydes was proposed by Mamardashvili *et al.*²⁴ who used triethyl orthoformate in TFA as the formylating reagent. 5,5'-Dicarboxy derivatives of dipyrrolylmethanes obtained by hydrogenolysis of dibenzyl esters are first dissolved 5–10 minutes after the completion of decarboxylation and triethyl orthoformate is added to the reaction mixture. This enters into the reaction with the 5,5'-unsubstituted dipyrrolylmethane formed. Apparently, a part of dipyrrolylmethane undergoes rearrangement.

The synthesis of dipyrrolylmethanes from pyrroles containing electron-withdrawing groups, *e.g.*, cyano groups, is of particular interest. This method was developed by Dolphin *et al.*⁴³ for the

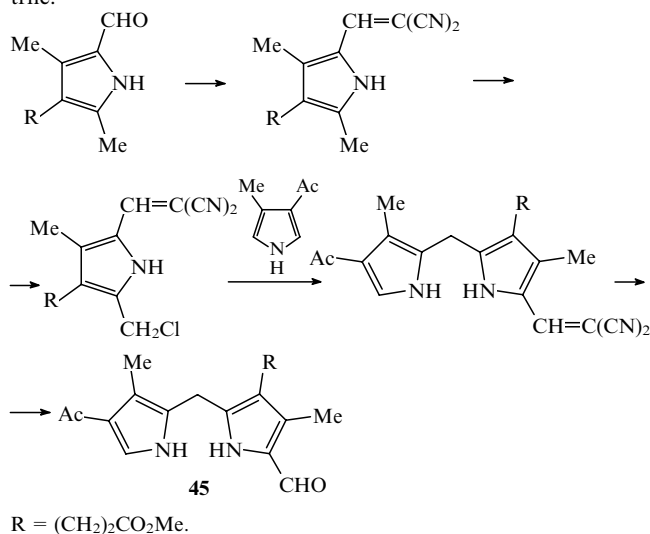
synthesis of bis(5-formyl-3,4-dimethylpyrrol-2-yl)methane. This reaction consists in the condensation of pyrroles **42** and **43** in dry dichloromethane in the presence of catalytic amounts of tin(IV) chloride resulting in dipyrrolylmethane **44**; its hydrolysis by heating on a water bath with a solution of KOH in aqueous ethanol gives a poorly soluble target dipyrrolylmethane. The yield of the final product can be significantly increased by performing deprotection in an inert atmosphere.



The synthesis of 5-formyl-5'-unsubstituted dipyrrolylmethanes deserves special attention. The first compound of this series, *viz.*, 3,3'-diethyl-5-formyl-4,4'-dimethyldipyrrol-2-ylmethane, was obtained by Dolphin *et al.*⁴⁴ using decarboxylation of

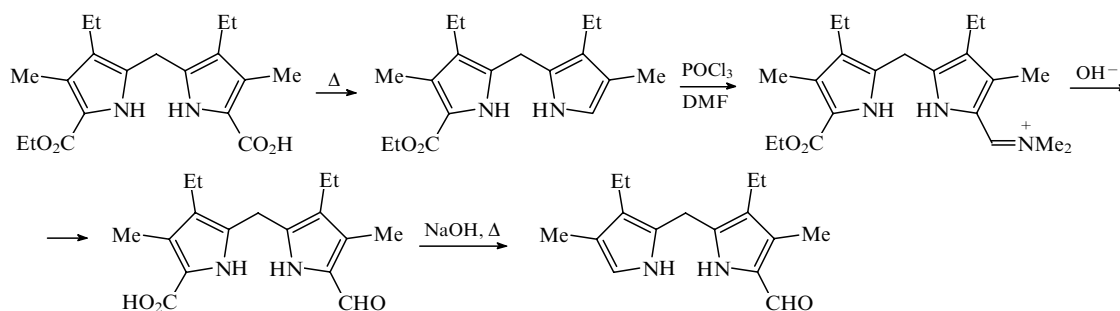
5-carboxy-5'-ethoxycarbonyl-3,3'-diethyl-4,4'-dimethyldipyrrol-2-ylmethane with subsequent Wilsmeier formylation of the resulting product (Scheme 4).

In the synthesis of the monoaldehyde **45**, the formyl group of the original pyrrole was protected by reaction with malononitrile.⁴⁵

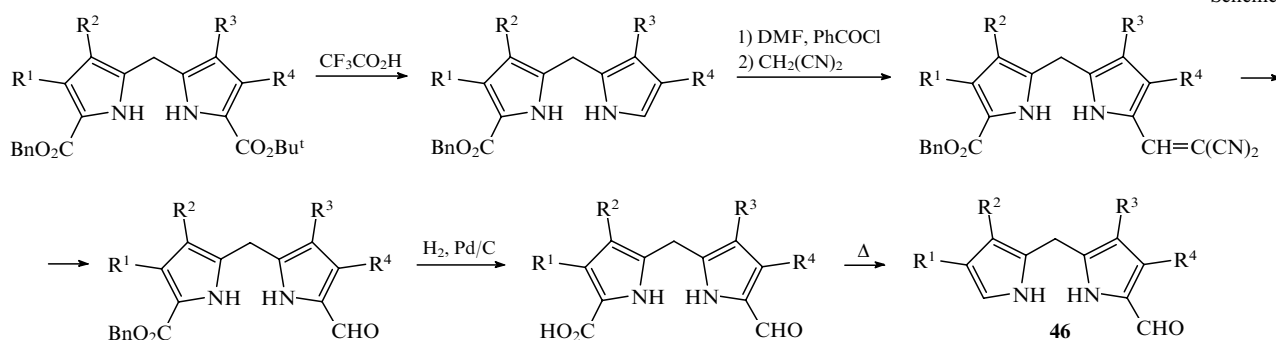


The monoformyldipyrrolylmethanes of the type **46** commonly employed in the synthesis of linear tetrapyrrolic compounds⁴² can be prepared from esters of the corresponding dicarboxylic acids using various approaches (Schemes 5 and 6).

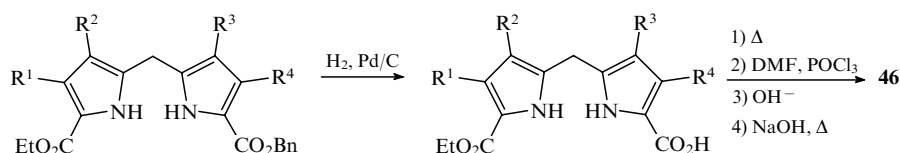
Scheme 4



Scheme 5



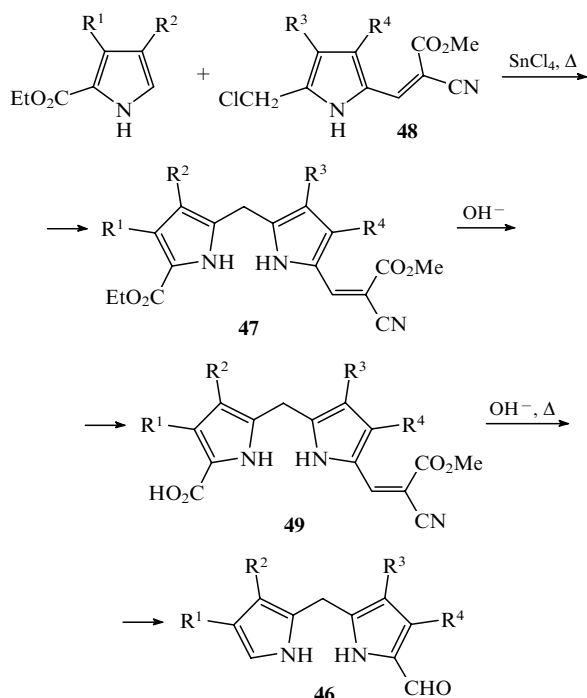
Scheme 6



Scheme 7

One of these approaches consists in thermal decarboxylation of intermediate 5-formyl-5'-carboxydipyrrolylmethanes; however, if the carboxypyrrolyl fragment contains electron-withdrawing groups, the reaction is carried out *via* iodo derivatives. The presence of even one electron-withdrawing aldehyde group increases the resistance of the methylene group of dipyrrolylmethane to oxidants and prevents intramolecular rearrangements, fragmentation and resinification. The monoformyldipyrrolylmethane **46** formed can be stored for a long period of time in a dry state in the absence of oxygen.⁴²

Unsymmetrical dipyrrolylmethanes **47** are formed in high yields in the reaction of α -ethoxycarbonyl-substituted pyrroles with compounds **48** containing chloromethyl and cyanovinyl (or cyanoacryl) groups in the α -positions. The latter deactivate pyrrole **48** and prevent its self-condensation. The condensation is carried out in inert solvents, *e.g.*, dichloromethane, dichloroethane, benzene, *etc.* The dipyrrolylmethanes of the type **49** are often decarboxylated upon heating with alkalis.⁴⁶ It should be noted that the cyanoacryl group which is hydrolysed more readily than the cyanovinyl group provides more efficient protection.

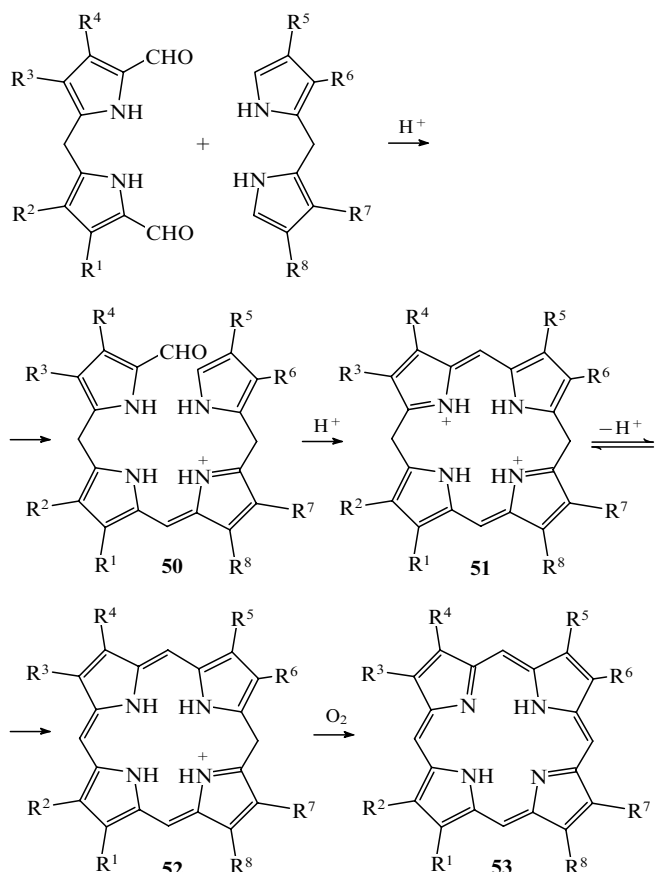


The common disadvantage of the syntheses based on monoformyl derivatives of dipyrrolylmethanes is the necessity to protect the aldehyde groups prior to chemical transformations.⁴⁶ Removal of protecting groups may provoke side reactions.

IV. Synthesis of porphyrins

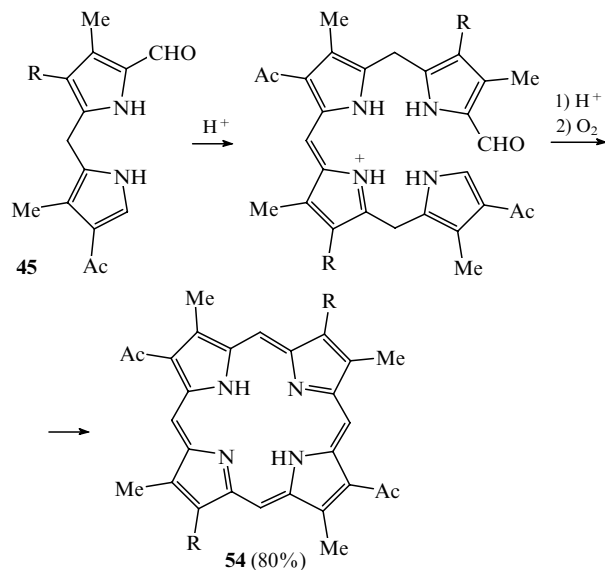
Dipyrrolylmethanes have been widely used in the synthesis of porphyrins since 1960. McDonald *et al.*³⁹ developed a procedure for the condensation of bis(5-formylpyrrol-2-yl)methanes with 5,5'-unsubstituted dipyrrolylmethanes under mild conditions. This reaction is carried out in glacial acetic acid in the presence of hydroiodic acid in a highly dilute solution (Scheme 7).

This process involves the formation of *b*-bilene **50** and porphodimethene **51** which is partially converted into phlorine **52**. Both the intermediate products and the phlorine **52** can be oxidised with atmospheric oxygen to yield porphyrin **53**. In some cases, self-condensation of the original bis(5-formylpyrrol-2-yl)methanes may occur to a certain extent. The yields of the porphyrins **53** prepared by condensation of symmetrical dipyrrolylmethanes by the method of McDonald are given in Table 2.



The condensation of bis(3-butyl-4-methylpyrrol-2-yl)methane with bis(3-butyl-5-formyl-4-methylpyrrol-2-yl)methane in ethanol in the presence of hydrobromic acid and subsequent oxidation of the reaction mixture with *o*-tetrachloroquinone results in 3,7,13,17-tetrabutyl-2,8,12,18-tetramethylporphyrin in 24% yield.⁹

A method for the synthesis of porphyrins from 5-formyl-5'-unsubstituted dipyrrolylmethanes has been proposed.⁴⁵ Self-condensation of compound **45** in glacial acetic acid in the presence of small quantities of acetic anhydride and hydrobromic acid gives 2,6-diacetyldeuteroporphyrin-II **54**.



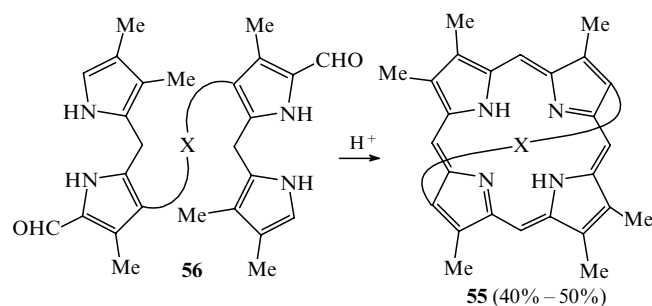
R = (CH₂)₂CO₂Me.

Table 2. The porphyrins **53** synthesised by the McDonald method.^{39, 47, 48}

R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶	R ⁷	R ⁸	Yield (%)
(CH ₂) ₂ CO ₂ Me	CH ₂ CO ₂ Me	CH ₂ CO ₂ Me	(CH ₂) ₂ CO ₂ Me	(CH ₂) ₂ CO ₂ Me	CH ₂ CO ₂ Me	CH ₂ CO ₂ Me	(CH ₂) ₂ CO ₂ Me	65
(CH ₂) ₂ CO ₂ Me	CH ₂ CO ₂ Me	CH ₂ CO ₂ Me	(CH ₂) ₂ CO ₂ Me	CH ₂ CO ₂ H	(CH ₂) ₂ CO ₂ H	(CH ₂) ₂ CO ₂ H	CH ₂ CO ₂ H	55
Me	CO ₂ Et	CO ₂ Et	Me	Me	CO ₂ Et	CO ₂ Et	Me	66
(CH ₂) ₂ CO ₂ Me	CH ₂ CO ₂ Me	CH ₂ CO ₂ Me	(CH ₂) ₂ CO ₂ Me	Me	CO ₂ Et	CO ₂ Et	Me	40
Me	CH=CH ₂	Me	CH=CH ₂	Me	(CH ₂) ₂ CO ₂ Me	(CH ₂) ₂ CO ₂ Me	Me	45
Me	CH(OH)CH ₂ CO ₂ Me	Me	CH(OH)CH ₂ CO ₂ Me	Me	(CH ₂) ₂ CO ₂ Me	(CH ₂) ₂ CO ₂ Me	Me	29 ^a
Et	Me	Et	Me	(CH ₂) ₂ CO ₂ Me	CH ₂ CO ₂ Me	CH ₂ CO ₂ Me	(CH ₂) ₂ CO ₂ Me	36 ^a

Note. The reaction was carried out in glacial acetic acid containing HI. ^a HCl was used instead of HI.

A series of sterically hindered (strapped) porphyrins **55** were synthesised by condensation of bisformyldipyrrolylmethanes **56** in a dichloromethane – methanol mixture (30 : 1) in the presence of *p*-toluenesulfonic acid.²⁷



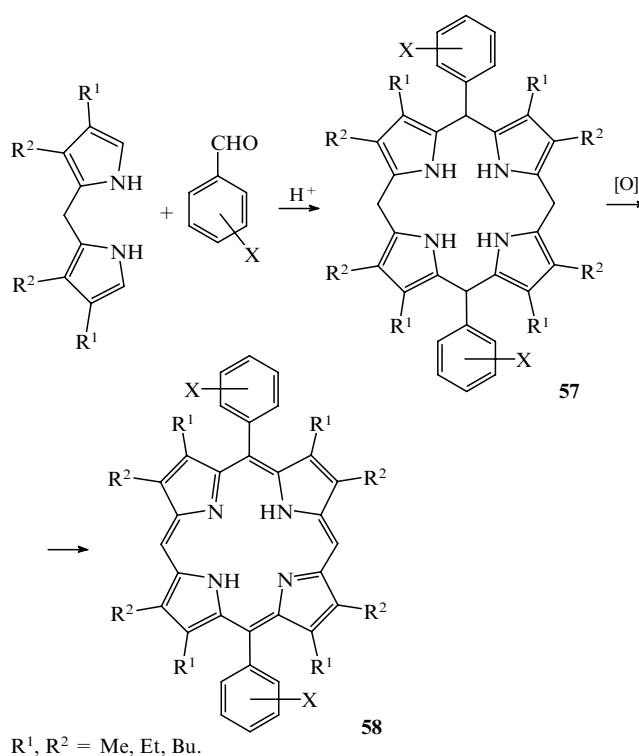
X is the residue of a saturated or an aromatic hydrocarbon.

Monoformyldipyrrolylmethanes have not found wide application in the synthesis of porphyrins due to their unavailability and the necessity to perform multistep syntheses.

The condensation of a symmetrical 5,5'-unsubstituted dipyrrolylmethane with triethyl orthoformate in formic acid was carried out.⁹ In this reaction, first the formylation of dipyrrolylmethane occurs followed by formation of the porphyrin. As this reaction occurs under drastic conditions, it can be accompanied by rearrangements of dipyrrolylmethane resulting in a mixture of isomeric porphyrins.

The condensation reactions of 3,3',4,4'-tetraalkyl-5,5'-unsubstituted dipyrrolylmethanes with aldehydes resulting in 5,15-dialkyl- and 5,15-diaryl derivatives of porphyrins are well documented in the literature.^{7–10} Initially, the oxidative condensation was carried out in one step, as in the case of synthesis of *meso*-tetraphenylporphyrins, *viz.*, in a boiling solvent in the presence of atmospheric oxygen.³³ In a pyridine – acetic acid mixture, the yield of porphyrins was rather low (~ 3%), but it was increased when the reaction was performed in benzene in the presence of TFA with high dilution of the reagents. It was shown^{49–52} that the use of a two-step procedure gives better results. The reaction of dipyrrolylmethane with benzaldehyde results in porphyrinogen **57**, which is further oxidised by benzoquinone derivatives to porphyrin **58**.

The yields of porphyrins **58** synthesised by this method are given in Table 3. The yield of porphyrin **58** (R¹ = Me, R² = Buⁿ, X = 2-OMe) does not depend on the solvating properties of the solvent (Table 4), which suggests high complexity of the reaction mechanism.⁵² The strength of the organic acid used as a catalyst only slightly affects the yield of the target product but the nature of the oxidant is a critical factor (Table 4). If the condensation is performed in a boiling solvent, the rate of the reaction is naturally increased with no decrease in the yield.⁵⁰



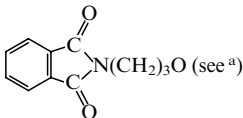
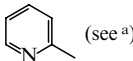
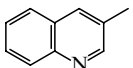
R¹, R² = Me, Et, Bu.

It is of note that rearrangements in dipyrrolylmethanes and/or intermediate tetrapyrroles in acid media result in the formation of monoarylporphyrins in addition to diarylporphyrins.³³ In some cases, the monosubstituted porphyrin is the main or even the only reaction product, especially at elevated temperatures. The nature of the substituent in the original dipyrrolylmethane and the presence of a *para*-substituent in the benzaldehyde molecule have little effect on the yield of the target porphyrins (Table 5).

The reaction of 5,5'-unsubstituted dipyrrolylmethanes with an equimolar mixture of two aromatic aldehydes gives unsymmetrical 5,15-diphenyloctaalkylporphyrins and a mixture of all the three feasible products, which have to be further separated by chromatography or, in some cases, by chemical modification. The closer are the electronic effects of the substituents in the aldehydes, the higher are the yields of unsymmetrical porphyrins.^{33, 53}

The condensation of the dialdehydes **59** with 5,5'-unsubstituted dipyrrolylmethanes affords 'capped' porphyrins **60** in sufficiently high yields.¹⁴ This method can be used for the synthesis of other complex systems containing octamethylporphyrin and etio-porphyrin fragments.^{13–16, 18, 22} Unfortunately, porphyrins containing methyl or ethyl groups in the β -positions of the macrocycle

Table 3. The conditions of synthesis and the yields of 5,15-diaryl(hetaryl)octaalkylporphyrins **58**.

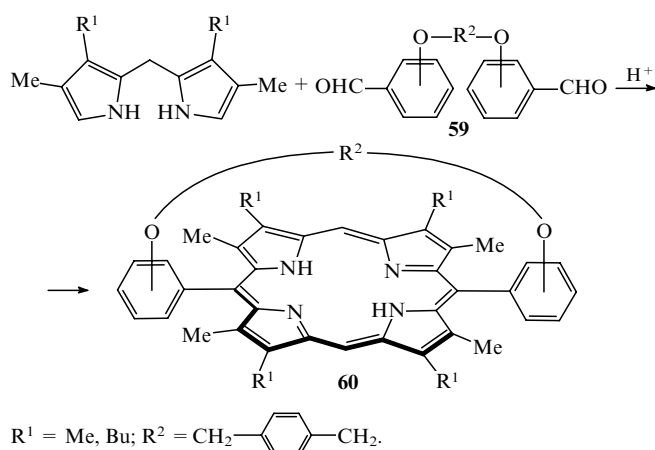
X	R ¹	R ²	Yield (%)	Solvent	Catalyst	Oxidant	Ref.
H	H	H	3	Py	AcOH	air	54
H	Me	Me	58	MeOH	CCl ₃ CO ₂ H	<i>p</i> -tetrachloroquinone	55
H	Me	Et	56	MeOH	CCl ₃ CO ₂ H	"	55
H	Et	Et	30	PhH	CF ₃ CO ₂ H	air	56
H	Me	Bu	11	MeOH	TsOH	<i>o</i> -tetrachloroquinone	32
2-Me	H	H	81	CH ₂ Cl ₂	CF ₃ CO ₂ H	<i>p</i> -tetrachloroquinone	55
2-Me	Et	Et	40	PhH	CF ₃ CO ₂ H	air	56
3-Me	H	H	86	CH ₂ Cl ₂	CF ₃ CO ₂ H	<i>p</i> -tetrachloroquinone	55
3-Me	Et	Et	30	PhH	CF ₃ CO ₂ H	air	56
4-Me	H	H	89	CH ₂ Cl ₂	CF ₃ CO ₂ H	<i>p</i> -tetrachloroquinone	55
4-Me	Me	Me	54	MeOH	CCl ₃ CO ₂ H	"	33
4-Me	Me	Et	56	MeOH	CCl ₃ CO ₂ H	"	33
4-Me	Me	Et	58	MeOH	TsOH	<i>o</i> -tetrachloroquinone	33
4-Me	Et	Et	30	PhH	CF ₃ CO ₂ H	air	56
3-Et	Me	Et	77	CH ₂ Cl ₂	CF ₃ CO ₂ H	DDQ	33
2-OMe	H	H	86	CH ₂ Cl ₂	CF ₃ CO ₂ H	<i>p</i> -tetrachloroquinone	55
2-OMe	Et	Et	30	PhH	CF ₃ CO ₂ H	air	56
3-OMe	Et	Et	40	PhH	CF ₃ CO ₂ H	"	56
4-OMe	H	H	83	CH ₂ Cl ₂	CF ₃ CO ₂ H	<i>p</i> -tetrachloroquinone	55
4-OMe	Me	Me	50	MeOH	CCl ₃ CO ₂ H	"	33
4-OMe	Me	Et	56	MeOH	CCl ₃ CO ₂ H	"	33
4-OMe	Et	Et	40	PhH	CF ₃ CO ₂ H	air	56
2,6-(OMe) ₂	Me	Et	6	MeCN	CCl ₃ CO ₂ H	<i>p</i> -tetrachloroquinone	57
							
4-OH	Me	Et	62	CH ₂ Cl ₂	CF ₃ CO ₂ H	"	58
2-Cl	H	H	80	CH ₂ Cl ₂	CF ₃ CO ₂ H	"	55
2,4-(Cl) ₂	H	H	79	CH ₂ Cl ₂	CF ₃ CO ₂ H	"	55
2-NO ₂	H	H	73	CH ₂ Cl ₂	CF ₃ CO ₂ H	"	55
4-NO ₂	Me	Me	69	MeOH	CCl ₃ CO ₂ H	"	55
4-NMe ₂	Me	Me	46	MeOH	CCl ₃ CO ₂ H	"	9
							
(see ^a)	Et	Et	55	MeOH	TsOH	<i>o</i> -tetrachloroquinone	59
							
(see ^a)	Et	Et	44	MeOH	TsOH	"	59

Note. DDQ is 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; ^a *meso*-substituent.

Table 4. The dependence of the yield of 5,15-diaryloctaalkylporphyrin **58** (R¹ = Me, R² = Buⁿ, X = 2-OMe) on the nature of the solvent, the catalyst and the oxidant.^{33, 50}

Solvent	Catalyst	Oxidant	Yield (%)
C ₆ H ₁₄	CF ₃ CO ₂ H	<i>o</i> -tetrachloroquinone	44
CCl ₄	CF ₃ CO ₂ H	"	24
PhH	CF ₃ CO ₂ H	"	27
CHCl ₃	CF ₃ CO ₂ H	"	40
MeCN	CF ₃ CO ₂ H	"	24
Et ₂ O	CF ₃ CO ₂ H	"	34
MeOH	CF ₃ CO ₂ H	"	37
Me ₂ CO	CF ₃ CO ₂ H	"	29
CHCl ₃	CCl ₃ CO ₂ H	"	44
CHCl ₃	CH ₂ ClCO ₂ H	"	44
CHCl ₃	CH ₂ ClCO ₂ H	<i>p</i> -tetrachloroquinone	32
CHCl ₃	CH ₂ ClCO ₂ H	<i>p</i> -tetrabromoquinone	28
CHCl ₃	CH ₂ ClCO ₂ H	DDQ	42

are poorly soluble in organic solvents, which significantly restricts their investigation and practical application.^{60–66}



Some attempts were undertaken to synthesise porphyrins with bulky alkyl substituents in the β- and *meso*-positions starting from

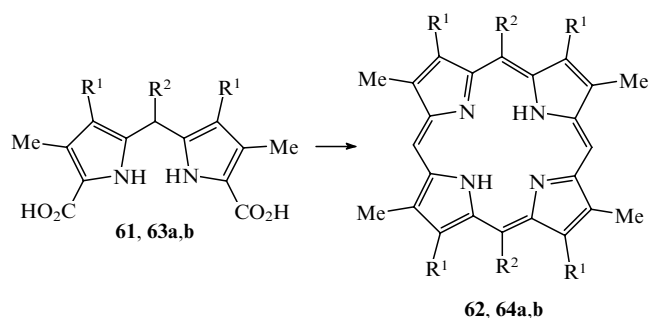
Table 5. The effects of substituents on the yields of 5,15-diaryloctaalkylporphyrins **58**.^{33, 50}

X	R ¹	R ²	Yield (%)
Solvent — MeOH			
H	Me	H	66
H	Me	Me	64
H	Me	Et	64
4-OMe	Me	Me	59
Solvent — CHCl ₃			
H	H	Me	61
H	Me	Me	68
H	Et	Me	33

5,5'-unsubstituted dipyrrolylmethanes aimed at enhancement of their solubilities.^{7–10, 24, 32, 67, 68} The yields of porphyrins in the reaction of bis(4-butyl-3-methylpyrrol-2-yl)methane with benzaldehyde in *o*-xylene–TFA, methanol–*p*-toluenesulfonic acid, chloroform–acetic acid systems and in acetic acid do not exceed 2.2%, 3%, 10% and 4.1%, respectively. In condensation of bis(dimethyl- and butylmethylpyrrol-2-yl)methanes with aliphatic aldehydes RCHO [R = Alk(C₂–C₇), C₁₁H₂₃] in TFA-containing chloroform followed by oxidation of the resulting porphyrinogens with *p*-tetrachloroquinone, the yield of porphyrins did not exceed 5%.⁹

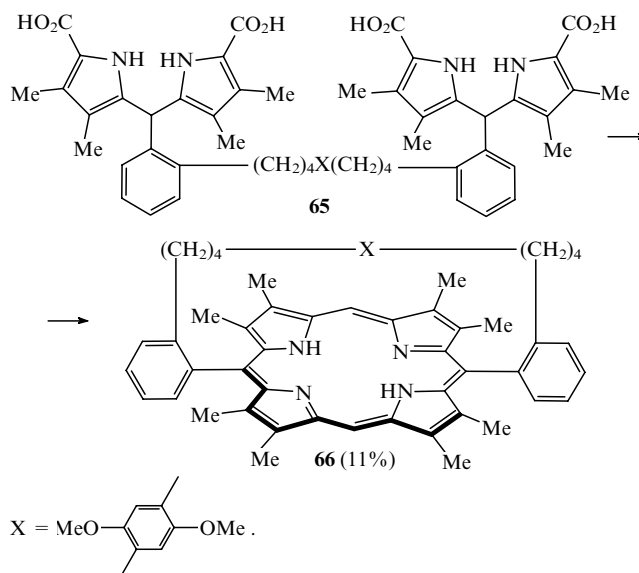
The synthesis of porphyrins from 5,5'-dicarboxy derivatives of dipyrrolylmethanes, the synthetic precursors of 5,5'-unsubstituted compounds and 5,5'-diformyldipyrrolylmethanes, appeared to be more efficient. 5,5'-Dicarboxylic acids are far more stable than 5,5'-unsubstituted derivatives, and porphyrins are formed from them in higher yields and the amounts of poorly separable admixtures are much less than in the synthesis of porphyrins from the corresponding unsubstituted and formyl derivatives of dipyrrolylmethanes.

Jackson *et al.*⁶⁹ were the first to carry out the condensation of dipyrrolylmethane **61** with triethyl orthoformate in dichloromethane in the presence of trichloroacetic acid. This reaction gives coproporphyrin-II **62** in 25% yield. A series of *meso*-disubstituted porphyrins were synthesised^{7, 8} by a modified Jackson–Kenner method.⁶⁹ In the condensation of 3,3'-dibutyl derivatives of *meso*-aryldipyrrolylmethanes **63a** with triethyl orthoformate in chloroform in the presence of TFA, the yield of porphyrins **64a** was the highest (~35%). The substitution of monochloroacetic acid for TFA decreases the yield to 17% and in the chloroform–acetic acid system the yield is 10%. The yield of porphyrins **64b** in the reaction of 3,3'-dimethyl derivatives of *meso*-alkyldipyrrolylmethanes **63b** with triethyl orthoformate in chloroform in the presence of TFA is 20%–25%.^{8, 10}

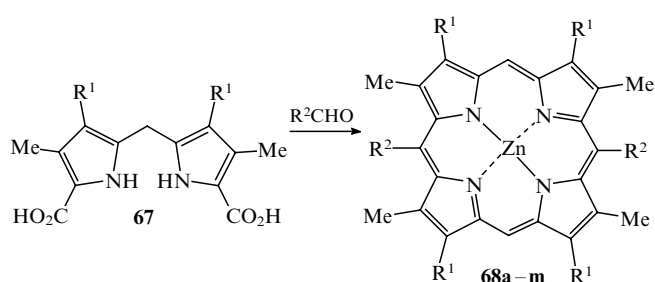


R¹ = (CH₂)₂CO₂Me, R² = H (**61**, **62**);
 R¹ = Bu; R² = Ph, C₆H₄OMe-2, C₆H₄OMe-3, C₆H₄OMe-4, C₆H₄NO₂-3, C₆H₄NO₂-4 (**63a**, **64a**); R¹ = Me; R² = Alk(C₁–C₇), C₁₁H₂₃ (**63b**, **64b**).

This method is widely used in the synthesis of 'capped' porphyrins.^{11, 27} For example, the cyclisation of bisdipyrrolylmethane **65** results in porphyrin **66**.¹¹ The methoxy groups in the substituent X in compound **66** were converted into the carbonyl groups by demethylation with boron tribromide in dichloromethane with subsequent oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (the yield of the target product is 54%).



As noted above, octamethyl derivatives of porphyrins manifest low solubility. However, the yield of porphyrins decreases drastically if the methyl groups are substituted by bulkier alkyl groups in order to increase the solubility. It was found³² that condensation of 5,5'-dicarboxy derivatives of dipyrrolylmethanes with aldehydes in pyridine in the presence of zinc acetate can increase the yield up to 20%. The highest yields are obtained with nitrobenzaldehydes, which can be attributed to the oxidising ability of the nitro group. Evidence in favour of this hypothesis can be derived from the increase in the yield of 5,15-diphenylporphyrin **68a** after addition of small quantities of nitrobenzene. The optimum ratio of the reagents (dipyrrolylmethane **67** : PhCHO : PhNO₂) is 1 : 3.6 : 3.6 (Fig. 1).



Compound 68	R ¹	R ²
a	Bu	Ph
b	Bu	C ₆ H ₄ OMe-4
c	Bu	C ₆ H ₄ OMe-3
d	Bu	C ₆ H ₄ OMe-2
e	Bu	C ₆ H ₄ NO ₂ -4
f	Bu	C ₆ H ₄ NO ₂ -3
g	Me	Me
h	Me	Et
i	Me	Pr
j	Me	Bu
k	Me	C ₅ H ₁₁
l	Me	C ₆ H ₁₃
m	Me	C ₁₁ H ₂₃

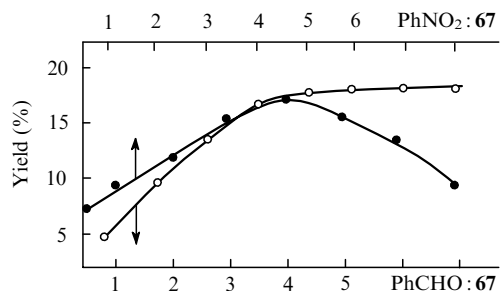
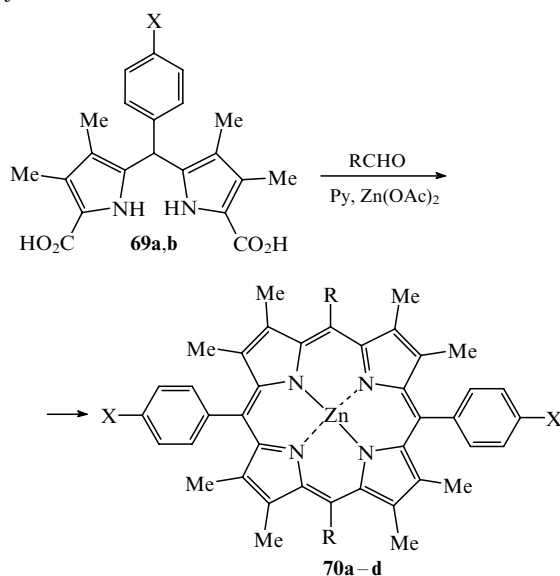


Figure 1. The dependence of the yield of porphyrin **68a** on the molar ratio of the reaction mixture components.

This method was used in the synthesis of 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-diphenylporphyrin (**68a**) and its derivatives **68b–f** containing different substituents in the benzene rings.^{9, 32, 65} The yields of porphyrins (~20%) practically do not depend on the nature of the substituent in the benzaldehyde. 2,8,12,18-Tetrabutyl-5,15-di(2-methoxyphenyl)-3,7,13,17-tetramethylporphyrin (**68d**) is an exception; its lower yield (10%) can be attributed to steric hindrance in the condensation of dipyrrolylmethane with 2-methoxybenzaldehyde. This porphyrin exists in the form of two atropoisomers (α,α and α,β), which differ in relative positions of substituents in the phenyl fragments relative to the macrocycle plane.

The reaction of dipyrrolylmethane **67** with aliphatic aldehydes in pyridine in an inert atmosphere (180 °C, 0.5–2 h) resulted in 5,15-dialkyl derivatives of octamethylporphyrin **68g–m**.⁶⁵ The presence of a coordinating reagent (zinc acetate) in the reaction mixture markedly facilitates the cyclocondensation. The yields of porphyrins **68g–m** are maximum at the $\text{Zn}(\text{OAc})_2$:dipyrrolylmethane **67**:RCHO molar ratio of 1.5:1:1.25. It is noteworthy that depending on the chain length of alkyl substituents, the yields of porphyrins vary in the range of 15%–33%, i.e., are relatively high (cf. tetraalkyl-substituted porphyrins, which are obtained by condensation of monopyrroles in 5% to 15% yields³³). A salient advantage of this method is that reaction products do not contain even trace amounts of *meso*-monosubstituted porphyrins.

The condensation of *meso*-aryl-substituted dipyrrolylmethanes **69a,b** with aliphatic aldehydes was used in the synthesis of 5,15-dialkyl-10,20-diaryl- β -octamethylporphyrins **70a–d**.²⁴ These compounds are characterised by high solubility due to the presence of *meso*-alkyl substituents; their aryl fragments can be subject to chemical modification.



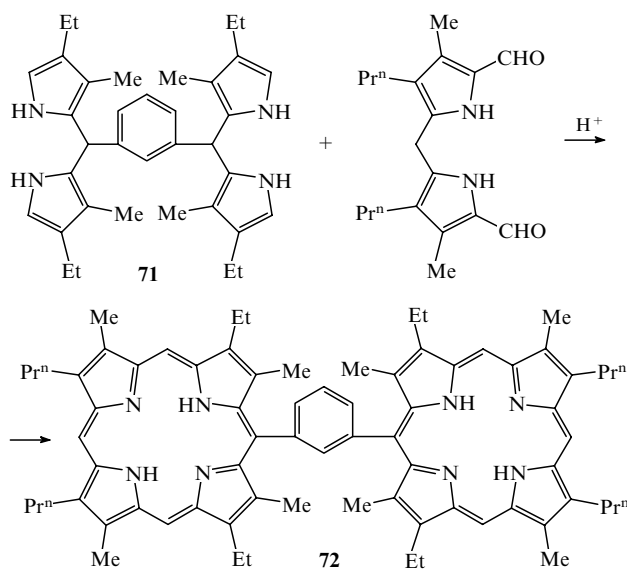
69: X = H (**a**), 4-OMe (**b**); **70:** X = H, R = Me (**a**), Et (**b**), C₆H₁₃ (**c**); X = 4-OMe, R = C₆H₁₃ (**d**).

The condensation of compounds **69a,b** with acetaldehyde and heptanal was carried out in pyridine at elevated temperatures and high pressures. The yields of *meso*-tetrasubstituted porphyrins **70a,c,d** are low (3% to 5%), which can be ascribed to steric hindrance in the cyclocondensation, and do not depend on the chain length of the alkyl substituent. Similarly, the yields of porphyrins obtained by the condensation of 5,5'-unsubstituted *meso*-aryldipyrrolylmethanes with benzaldehyde and formaldehyde are 5%–6% and do not depend on the nature of the aldehyde.²⁴

It may thus be concluded that 5,5'-dicarboxy derivatives of dipyrrolylmethanes are promising reagents in the synthetic chemistry of porphyrins. They compare favourably with 5,5'-unsubstituted dipyrrolylmethanes and formyl derivatives by relative accessibility and, which is particularly important, by their resistance to oxidation. These compounds can be used in the synthesis of porphyrins of complex structure, including position isomers.

V. Synthesis of bisporphyrins

A vast variety of bisporphyrins with different spatial arrangement of macrocycles have been synthesised from dipyrrolylmethanes. Such syntheses are typically performed by a modified McDonald method.^{11, 13, 15, 16, 70} Sessler *et al.*¹² were the first to synthesise the so-called 'gable' bisporphyrins the porphyrin fragments in which are linked through the *meta*-positions of the benzene ring. This synthesis involves the formation of intermediate dipyrrolyl structures. The reaction of compound **71** with 5,5'-diformyl derivatives of dipyrrolylmethane in methanol in the presence of *p*-toluenesulfonic acid and subsequent oxidation of the condensation product with tetrachloroquinone result in bisporphyrin **72**.¹⁵

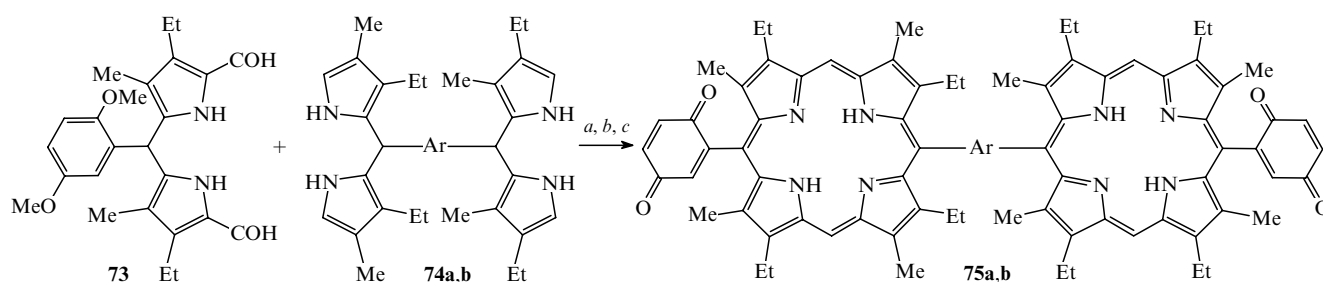


In order to construct models which are geometrically identical to the active centres involved in photosynthesis, Sessler *et al.*¹⁶ carried out the condensation of the 5,5'-diformyl derivative of dipyrrolylmethane **73** with bisdipyrrolylmethanes **74a,b** to yield bisporphyrin **75a** with spatially approximated porphyrin nuclei and its linear analog **75b**. The same procedure was used in the synthesis of a bisporphyrin in which the porphyrin macrocycles were linked through a quinone fragment. The yield of porphyrins in the first stage of this reaction was ~5% (Scheme 8).

The synthesis of compounds in which porphyrin fragments are linked by aromatic bridges, which stabilise their spatial structure has been described.¹³ This synthesis consisted in the condensation of bisdipyrrolylmethanes **76** with bis(5-formyl-3,4-dimethylpyrrol-2-yl)methane and resulted in bisporphyrins **77** (Scheme 9).

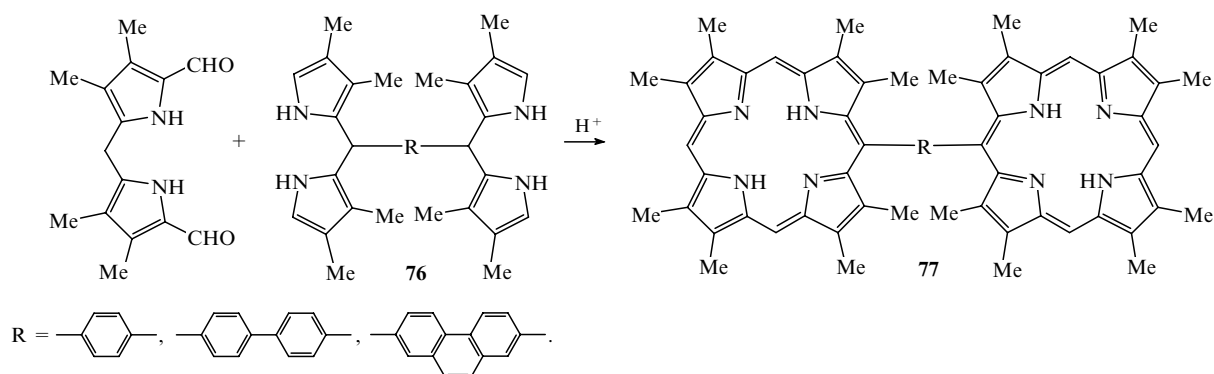
The reaction of bis(5-formyl-3,4-dimethylpyrrol-2-yl)methane with stereoisomeric bisdipyrrolylmethanes **78** in methanol in the presence of *p*-toluenesulfonic acid and subsequent oxidation

Scheme 8

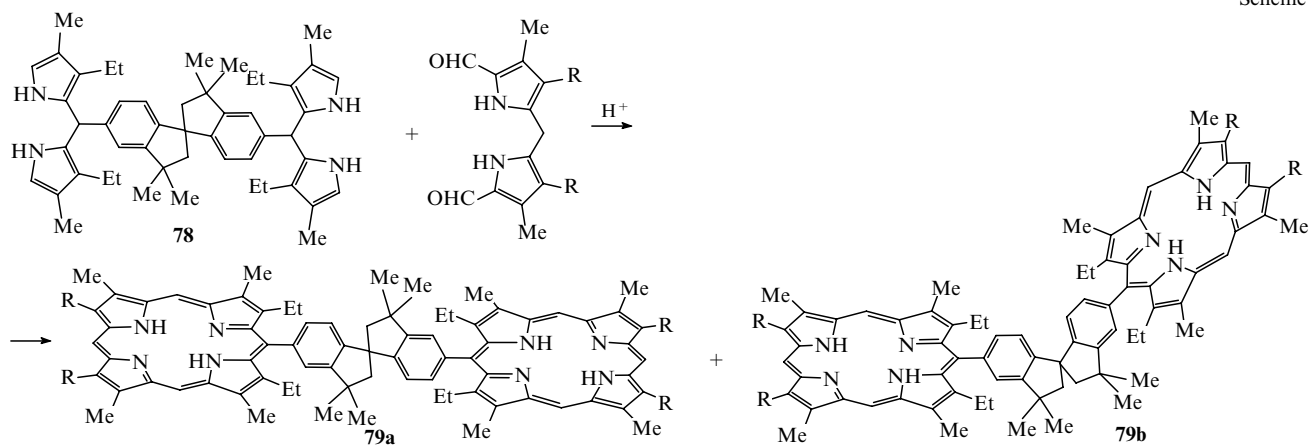


$\text{Ar} = m\text{-C}_6\text{H}_4$ (**a**), $p\text{-C}_6\text{H}_4$ (**b**); (a) H^+ ; (b) BBr_3 , CH_2Cl_2 ; (c) $[\text{O}]$.

Scheme 9



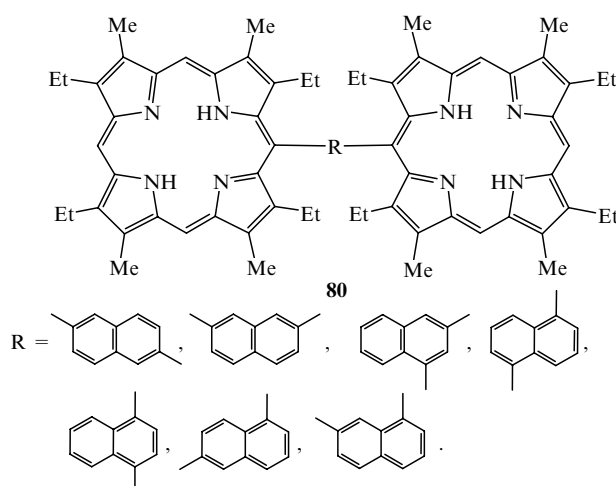
Scheme 10



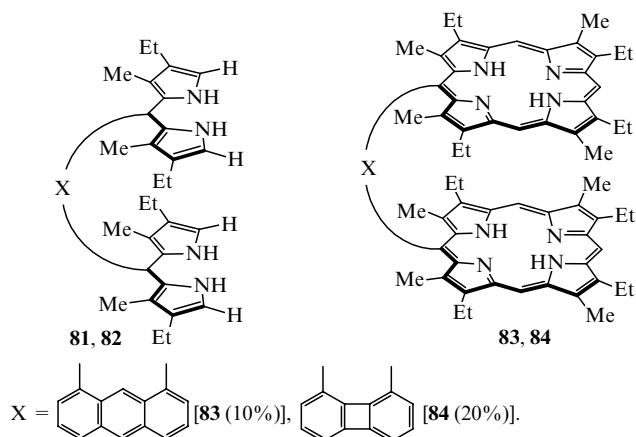
$\text{R} = \text{C}_6\text{H}_{13}$.

of the reaction mixture with tetrachloroquinone afforded spiro derivatives **79a,b** in a total yield of 5% (Scheme 10).^{22, 70} Owing to the presence of a rigid spirobisindane bridge between the macrocycles, bisporphyrins acquired fixed spatial orientation. The distances between the centres of the macrocycles are equal to 1.80 and 1.00 nm, respectively; the porphyrin fragments of compound **79b** partially overlap at an angle (see Scheme 10).

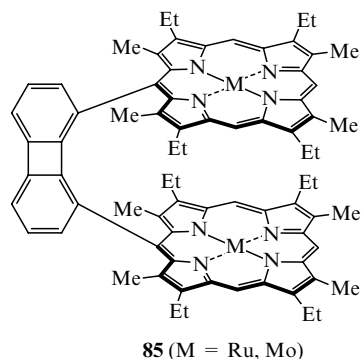
Osuka and Maruyama⁷¹ synthesised a series of bisporphyrins **80** the porphyrin fragments of which were linked through different positions of the naphthalene nucleus. The original 5,5'-unsubstituted bisdipyrrolylmethanes were prepared by the reaction of 5-unsubstituted pyrrole with the corresponding dialdehydes according to the known procedure.¹³ The naphthalene fragments ensure rigid binding of porphyrin macrocycles, which are perpendicular to their plane.



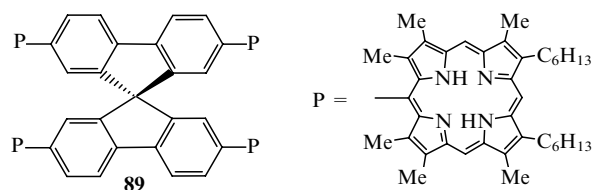
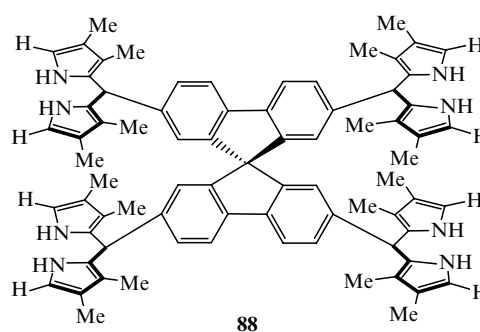
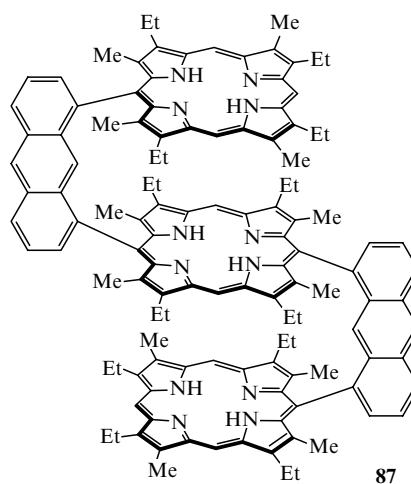
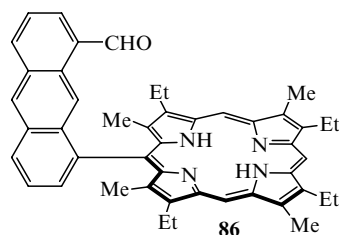
A series of bisporphyrins with a 'face-to-face' orientation of fragments (FTF-porphyrins) containing a conformationally rigid backbone between the macrocycles has been synthesised.^{18, 72, 73} The reaction of bisdipyrrolylmethane **81** with bis(3-ethyl-4-methyl-5-methoxymethylpyrrol-2-yl)methane in boiling benzene with its subsequent oxidation with tetrachloroquinone or the reaction of compound **82** with bis(3-ethyl-5-formyl-4-methylpyrrol-2-yl)methane in methanol in the presence of perchloric acid yields bisporphyrins **83** and **84**.



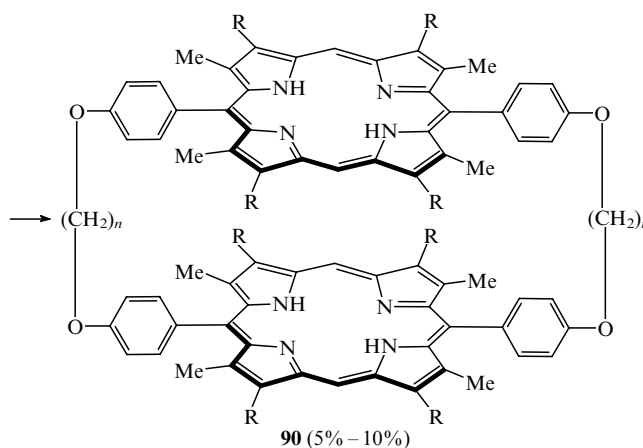
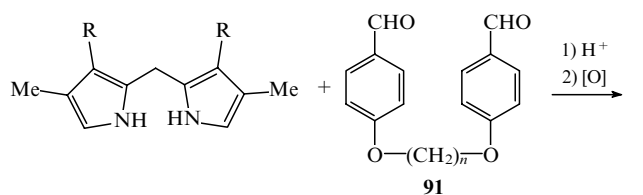
It has been noted^{18, 72} that bisporphyrins **83** and **84** are devoid of stereoisomers. Spectral data provide evidence in favour of the FTF-orientation of the macrocycles. Collman *et al.*⁷⁴ synthesised binuclear ruthenium and molybdenum complexes **85**, which generate coordination compounds with intramolecular metal–metal bonds upon photolysis in pyridine.



The condensation of formylanthrylporphyrin **86** with bis(3-ethyl-4-methylpyrrol-2-yl)methane has led to a compound of the FTF-type (**87**).¹⁷ Osuka *et al.*⁷⁵ carried out the synthesis of tetrakisporphyrin **89** from compound **88** and bis(5-formyl-3-hexyl-4-methylpyrrol-2-yl)methane under identical conditions.



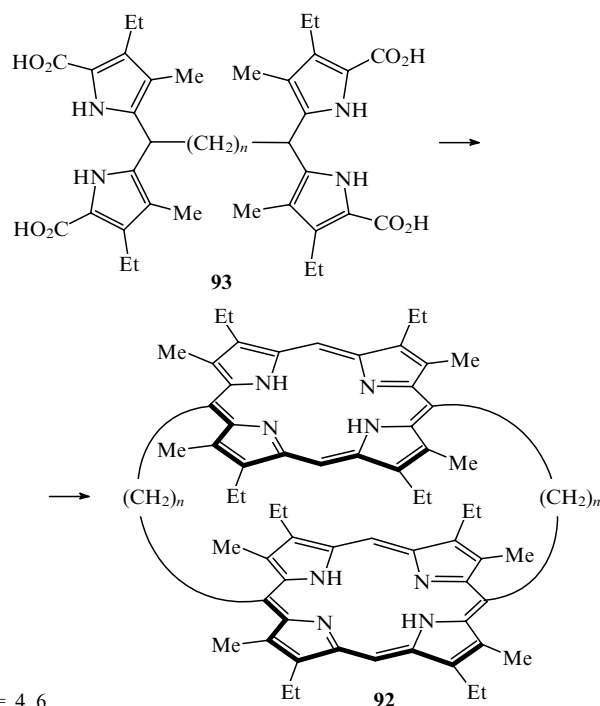
A two-step synthesis of cyclophanes **90** containing two bridging $\text{O}(\text{CH}_2)_n\text{O}$ groups connecting the *p*-positions of the benzene nuclei, has been described.^{76–78} The condensation of dialdehydes



R = Et, Bu; $n = 2-4$.

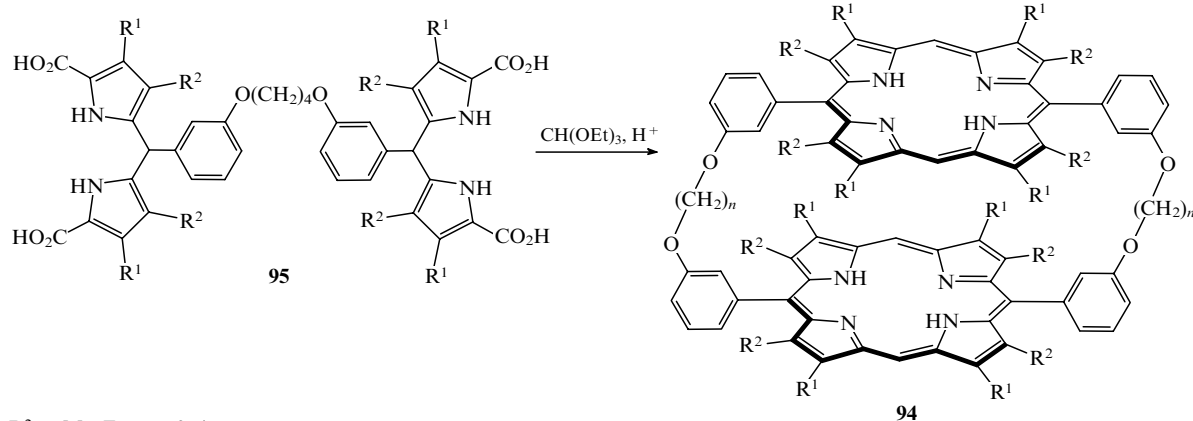
91 with dipyrrolylmethanes was carried out in TFA-containing acetonitrile in an atmosphere of nitrogen. The freely soluble porphyrinogens formed were oxidised *in situ* with *o*-tetrachloroquinone. Cyclophane **90**, the only reaction product, could be easily separated from admixtures by column chromatography.

5,5'-Dicarboxy derivatives of dipyrrolylmethanes were also used in the synthesis of bisporphyrins. The procedure used by Collman⁷⁹ in the synthesis of cyclophanes **92** linked with the bridging (CH₂)_n (*n* = 4, 6) groups through the *meso*-positions is a modification of the Jackson–Kenner synthesis.⁶⁹ Heating of bisdipyrrolylmethanes **93** (*n* = 4, 6) with triethyl orthoformate in dichloromethane in the presence of trichloroacetic acid results in the formation of compounds **92** in very low yields.



The same procedure was used^{80–82} in the synthesis of cyclophanes **94** in which bridging groups connect the *meta*-positions of the benzene nuclei. They were synthesised by the reaction of bisdipyrrolylmethanes **95** with triethyl orthoformate in boiling chloroform containing 2% TFA. The yield of compound **94** was ~ 5%; the monomeric porphyrins were not formed.

Cyclophane **94** exists in the form of three atropoisomers (their structures are shown in Fig. 2). In bisdipyrrolylmethanes, the phenoxy groups easily rotate around the C–C bond of the bridges, thus giving rise to one or another spatial isomer depending on their orientation at the moment of cyclisation. The calculation of the structure of octamethyl analogues carried out by the molecular mechanics method⁸² confirmed the possibility of



R¹, R² = Me, Et; *n* = 3, 4.

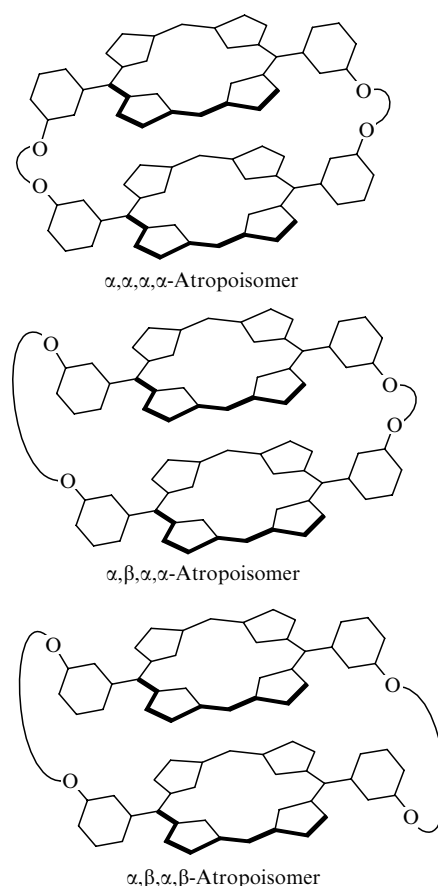
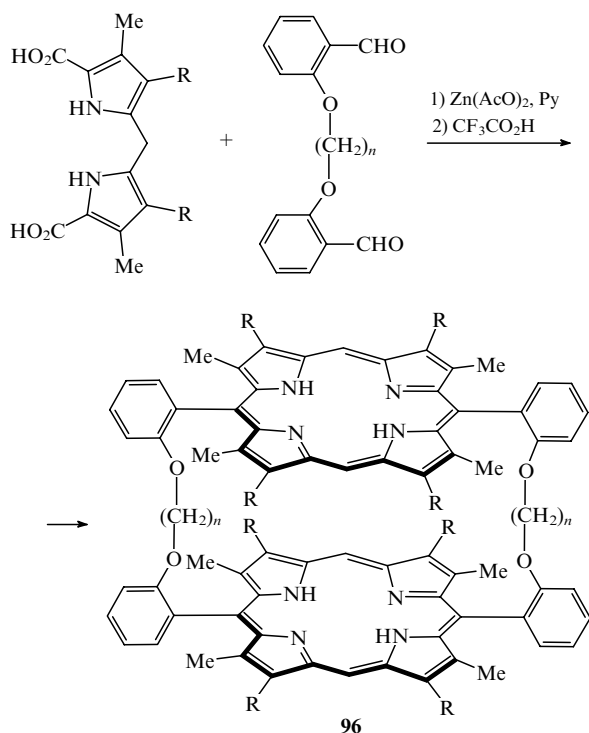


Figure 2. The atropoisomers of cyclophane **94** containing two conformationally active ester bridges.

existence of $\alpha, \alpha, \alpha, \alpha$ -, $\alpha, \beta, \alpha, \alpha$ - and $\alpha, \beta, \alpha, \beta$ -atropoisomers. The insufficient length of bridging groups excludes the formation of the $\alpha, \alpha, \beta, \beta$ -isomer. Atropoisomers manifest different mobility in thin-layer chromatography (pyridine–hexane, 1:4) which allowed their separation. The assignment of atropoisomers was performed on the basis of ¹H NMR data as well as on the basis of analysis of their coordination properties and chromatographic behaviour.⁸⁰

A simpler procedure for the synthesis of analogous compounds has been proposed.⁷⁶ The condensation of 5,5'-dicarboxy-substituted dipyrrolylmethanes with dialdehydes in pyridine in the presence of zinc acetate resulted in cyclophanes **96** (which can also exist in the form of three atropoisomers) with

bridging $\text{O}(\text{CH}_2)_n\text{O}$ ($n = 2-4$) groups connecting the *ortho*-positions of the benzene rings.



$R = \text{Et, Bu}; n = 2-4$.

The zinc complexes formed by template synthesis were destroyed *in situ* by treatment with TFA. The molar ratio of the reaction mixture components is critical for the yields of cyclophanes **96**. Using the mathematical simulation method, it was demonstrated that the maximum yield of these compounds varied from 8% to 15% and was reached at the dipyrrolylmethane : dialdehyde : zinc acetate molar ratio of 1 : 2 : 1. These yields decrease regularly with a decrease in the number of methylene units, n . The same applies to cyclophanes which contain bridging groups connecting the *meta*- and *para*-positions of the benzene nuclei (compounds **90** and **94**) and may occur as a result of stronger spatial restrictions in cyclocondensation. The optimum duration of the reaction is 2.5 to 3 h. With a drop in temperature from 120 to 80 °C, the reaction products contain only trace amounts of cyclophanes.

It should be noted that the cyclophane **96** containing a shortened bridge $\text{O}(\text{CH}_2)_2\text{O}$ cannot form isomers; all the oxygen atoms of the ether group are arranged inwards towards the interporphyrin cavity.

Cyclophanes containing methyl and ethyl groups in the β -positions of the macrocycles are extremely poorly soluble in the majority of organic solvents; tetrabutyl derivatives are more soluble.

VI. Conclusion

The use of dipyrrolylmethanes opens up good perspectives for the synthesis of different types of mono- and bisporphyrins. At the same time, the potentialities of syntheses based on dipyrrolylmethanes are far from being exhausted. These methods hold a prominent place in the synthetic chemistry of porphyrins. The choice of particular synthetic procedures is largely determined by the symmetry of the porphyrin molecule, the mode and mutual arrangement of substituents in the macrocycle as well as by the availability of the starting compounds.

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Synthesis, structure and properties of coordination compounds of iron phthalocyanines and their analogues

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Abstract. Methods for the synthesis of various coordination compounds of iron phthalocyanines and their closest structural analogues, *viz.*, iron porphyrazines and naphthalocyanines, their structures, properties and applications are surveyed. The bibliography includes 230 references.

I. Introduction

Haem-containing biological systems play a unique role in living nature. These systems are involved in oxygen binding and transport (haemoglobin and myoglobin) and in catalysis of vital reactions (oxygenases, catalases, peroxidases and cytochromes).^{1,2}

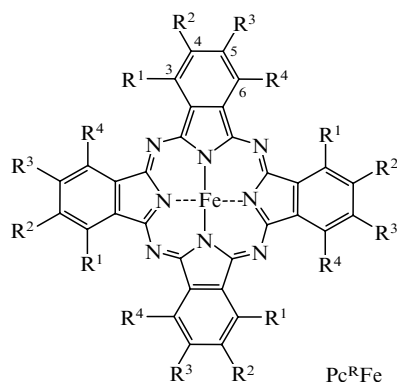
The closest synthetic analogues of porphyrins, *viz.*, phthalocyanines (tetraazatetrabenzoporphins) and related compounds, find wide applications primarily as dyes, pigments and catalysts of oxidative desulfurisation of hydrocarbons.^{3,4} In recent years, these compounds have also been examined and used as components of gas sensors, electrochromic materials, passive laser valves and isolators for amplifying stages of solid-state and chemical lasers. These compounds have also found use as antimicrobial agents and photosensitisers in the photodynamic therapy of cancer.⁵ In the last decades, catalysts exhibiting high oxidase and peroxidase activities have been constructed based on phthalocyanines.³ Iron-containing complexes have particular promise. Increased scientific and practical interest in these complexes stems from the fact that they are characterised by a great diversity of coordination and redox forms.^{6–11} In spite of the fact that different aspects of chemistry and applications of iron phthalocyanines

and their analogues have been considered in a great number of publications and patents, many questions about the structures and the valent and spin states of the major coordination forms of these compounds remain as the subjects of discussion.

The properties and applications of selected coordination forms of complexes of iron phthalocyanines and their analogues have been surveyed in several fundamental reviews.^{3,4,9–11} However, the systematic analysis of a wide range of these compounds is lacking in the literature. In the present review, modern data on the synthesis and coordination chemistry of iron phthalocyanines and their analogues are considered and analysed.

II. Synthesis and properties of iron phthalocyanines and their analogues

In 1928, chemists from the 'Scottish Dyes Ltd.' found a dark-blue compound deposited on the walls of a reactor in the synthesis of phthalimide from phthalic anhydride and ammonia. This compound was extremely stable with respect to acids and alkalis, and it was suggested that it has the structure of PcFe (Pc^RFe , where $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{R}^4 = \text{H}$) based on the results of a detailed study of its properties and structure.



As a result, a new class of macrocyclic tetrapyrrole compounds, *viz.*, phthalocyanines, has been discovered.^{15–17} The synthesis of PcFe was described in detail for the first time in the classical papers of Linstead.^{16,17} Presently, PcFe and its numerous R -substituted derivatives (Pc^RFe) are prepared by reactions of various derivatives of phthalic acid with iron or its compounds, which are often performed in the presence of catalysts (Scheme 1). In all cases, the reactions are carried out either in a melt of the reagents (the sintering method) or in high-boiling organic sol-

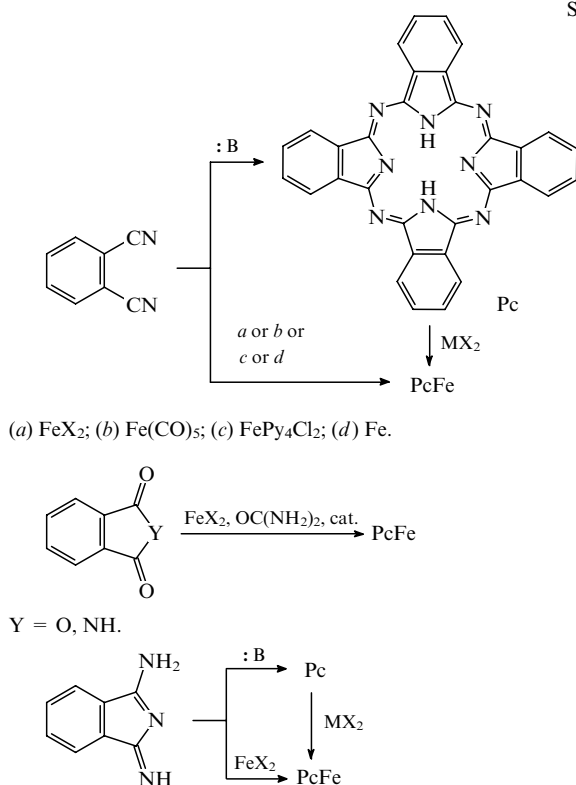
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Scheme 1



vents.^{3, 4, 10, 11} Thus heating of phthalonitrile with iron(II) hydroxide in trichlorobenzene containing 10% of quinoline afforded PcFe in 73% yield.¹⁸ Boiling of phthalonitrile with iron pentacarbonyl in 1-chloronaphthalene gave PcFe in 50% yield. In the latter case, there was virtually no need for further purification of the product.^{19, 20} The syntheses of PcFe from phthalonitrile and FePy_4Cl_2 (in yields of up to 70%)²¹ or from phthalic anhydride, urea and powdered iron (or its compounds) in the presence of different catalysts (boric acid, ammonium molybdate or titanium chloride) (in yields of up to 65%) were described; however, the purities of the final product were often not reported.^{22–24} Iron phthalocyanine can also be synthesised by metallation of metal-free phthalocyanine (Pc) prepared from the diimino derivative of isoindolinedione or phthalonitrile in the presence of a base (:B). A convenient procedure for the preparation of PcFe and its derivatives by heating the reagents with the use of microwave radiation

was proposed.²⁵ The latter procedure afforded the highly pure (up to 97%) target product in high yields (up to 80%). Iron phthalocyanine was also formed as a result of macrocycle contraction in the reaction of the so-called uranyl superphthalocyanine, which is a pentadentate analogue of phthalocyanine, with iron salts.²⁶ Substituted iron phthalocyanines are synthesised according to procedures virtually identical to those used for the preparation of PcFe. Complexes Pc^RFe containing different numbers of substituents R, where R is the halogen atom or the alkyl, aryl, nitro, alkoxy, aryloxy, alkylthio, arylthio, arylsulfonyl, polyfluoroalkoxy, polyfluorosulfamoyloxy, carboxy, sulfo, *etc.* groups, were described in the literature.^{4, 6–8, 27–36}

Final purification of complexes was carried out by high-temperature sublimation *in vacuo* or by removal of ligands (L) from bisaxially coordinated complexes of the general formula Pc^RFeL_2 on heating *in vacuo* or under a stream of an inert gas.^{6–14}

Polymeric compounds containing the PcFe fragments can be prepared in a way analogous to that for the preparation of substituted iron phthalocyanines.^{37–40} The formation of polymeric PcFe by the reaction of pyromellitic acid, an iron salt and urea in the presence of a catalyst was studied in detail.⁴⁰ The Mössbauer spectra of the resulting polymer contain four doublets belonging to polymeric and monomeric complexes as well as to oxidation products containing the phthalocyanine fragments. After purification of the polymer by gel permeation chromatography and its heating to 300 °C, the Mössbauer spectra exhibit only one doublet with the parameters characteristic of the $[\text{PcFe}^{\text{II}}]_n$ complex.

Like the majority of phthalocyanine complexes with other metals, PcFe can occur in different crystal modifications.^{4, 12, 14} According to the data from X-ray diffraction analysis, the environment about the iron ion in one of these modifications, *viz.*, in the β -modification of PcFe, is a pseudooctahedron formed by four isoindole nitrogen atoms of the virtually planar phthalocyanine ligand and two *meso*-nitrogen atoms of the adjacent PcFe molecules (Table 1).⁴¹ The magnetic moments (μ_{eff}) for different specimens of PcFe at room temperature are in the range of 3.7–4.5 μ_{B} .^{51–53} The Mössbauer spectra of a series of Pc^RFe complexes in which the σ -donor and π -acceptor properties of the peripheral substituents vary over a rather wide range were examined (Table 2). The parameters of the Mössbauer spectra δ and ΔE_{Q} for these complexes, which reflect the character of the Pc–Fe interaction, should correlate with the Hammett constants (σ). However, with the aim of giving an adequate account of the effect of substituents in the phthalocyanine macrocycle on the Mössbauer parameters, the authors^{27, 28} had to introduce two arbitrary additional parameters describing the σ -donor and π -acceptor properties of the substituents (Σ and Π , respectively).

Table 1. Structures of iron phthalocyanine, its biaxially coordinated complexes and their analogues established by X-ray diffraction studies.

Complex	Oxidation state of iron	Coordination polyhedron	Bond lengths /Å		Ref.
			Fe–N(Pc)	Fe–L	
PcFe	+2	N ₄	1.926, 1.927		41
$[\text{PcFe}]^-$	+1/+2	N ₄	1.910		42
$[\text{PcFe}]^{2-}$	+1/+2	N ₄	1.910		42
$\text{PcFe}(\text{DMSO})_2$	+2	N ₄ S ₂	1.931, 1.951	2.308	43
$\text{PcFe}(4\text{-MeC}_5\text{H}_4\text{N})_2$	+2	N ₆	1.932, 1.937	2.040	44
$\text{PcFe}(\text{MeIm})_2$	+2	N ₆	1.926, 1.955	1.946	45
$\text{PcFe}(4\text{-MeC}_5\text{H}_{10}\text{N})_2$	+2	N ₆	1.929, 1.930	2.119	46
$\text{PcFe}(\text{CO})(\text{DMF})$	+2	N ₄ OC	1.889	1.72 (CO), 2.07 (O)	47
$1,2\text{-NcFe}(\text{cyclo-C}_6\text{H}_{11}\text{NC})_2$	+2	N ₄ C ₂	1.936, 1.949	1.911	48
$1,2\text{-NcFe}(\text{Bu}^t\text{NC})_2$	+2	N ₄ C ₂	—	1.913	49
$\text{PNP}[\text{PcFe}(\text{CN})_2]$	+3	N ₄ C ₂	1.939, 1.957	1.976	50

Note. MeIm is *N*-methylimidazole, 1,2-NcFe is iron 1,2-naphthalocyanine, 1,2-Nc^tFe is tetrakis(7-*tert*-butyl)-substituted 1,2-NcFe, PNP is the triphenylphosphineimmonium cation.

Table 2. Parameters of Mössbauer spectra of the $\text{Pc}^{\text{R}}\text{Fe}$ complexes.

R^1	R^2	R^3	R^4	T/K	δ^{a} /mm s $^{-1}$	ΔE_{Q} /mm s $^{-1}$	Ref.
H	H	H	H	4.2	0.48	2.70	28
				111	0.736 ^b	2.601	54
				163	0.691 ^b	2.609	
				203	0.667 ^b	2.604	
H	$\text{CO}_2\text{C}_{10}\text{H}_{21}$	H	H	298	0.634 ^b	2.581	
				4.3	0.29	2.78	28
				78.8	0.29	2.71	
				298	0.22	2.61	
H	$\text{CO}_2\text{C}_{10}\text{H}_{21}$	$\text{CO}_2\text{C}_{10}\text{H}_{21}$	H	4.2	0.23	2.48	28
				79.3	0.20	2.50	
				298	0.17	2.48	
				4.3	0.30	1.96	28
H	$\text{C}(\text{O})\text{N}(\text{C}_{10}\text{H}_{21})\text{C}(\text{O})$	H	H	79.3	0.27	1.96	
				298	0.16	1.96	
				4.3	0.22	1.99	28
				78.5	0.22	1.99	
Cl	Cl	Cl	Cl	298	0.15	2.00	
				4.5	0.32	1.72	28
				78.7	0.32	1.65	
				291	0.25	1.69	
H	CN	CN	H	4.3	0.27	1.56	28
				79.0	0.27	1.56	
				298	0.20	1.56	
				5.1	0.49	2.66	27
H	Me	Me	H	79	0.48	2.67	
				297	0.38	2.58	
				4.6	0.47	2.88	27
				79	0.47	2.80	
H	OCH_2O	H	H	292	0.37	2.61	
				4.2	0.48	2.54	27
				79	0.46	2.53	
				297	0.33	2.49	
H	Bu^{t}	H	H	79	0.43	2.42	27
				4.2	0.28	2.91	27
				79	0.28	2.91	
				299	0.20	2.53	
H	SPh	H	H	4.4	0.24	1.38	27
				79	0.23	1.37	
				296	0.14	1.36	
				77	0.238	2.554	9
H	CO_2H	CO_2H	H	293	0.137	2.498	
				77	0.297	2.923	9
				4.3	0.47	2.36	27
				79	0.46	2.31	
H	CO_2H	$(\text{CH}_2)_4$	H	299	0.37	2.28	
				293	0.36	2.21	55

^a Relative to metallic iron; ^b relative to sodium nitroprusside.

The Σ value is larger for stronger σ -donors, whereas the Π value is larger for stronger π -donor and weaker π -acceptor. The Mössbauer parameters are related to the Σ and Π constants by the following equations:

$$\delta = -\Sigma + \Pi,$$

$$\Delta E_{\text{Q}} = a\Sigma - b\Pi + c,$$

where a , b and c are constants and $a > b > 0$. The Mössbauer spectra of all the $\text{Pc}^{\text{R}}\text{Fe}$ complexes studied are characterised by high and virtually temperature-independent quadrupole splitting (see Table 2) typical of iron(II) complexes with the intermediate ($S = 1$) spin state.^{27, 28, 41, 51}

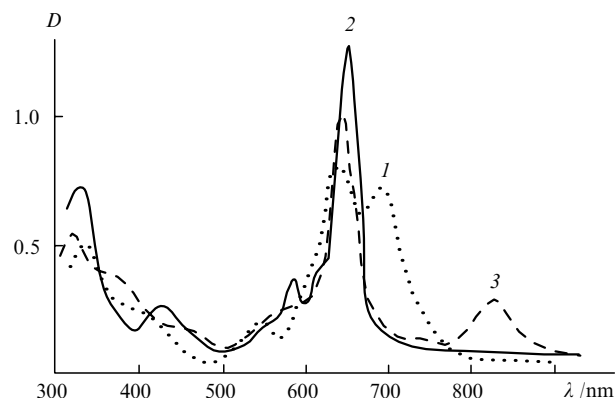
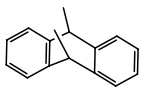


Figure 1. Electronic absorption spectra of iron(II) tetrakis(4-*tert*-butyl)phthalocyanine (Pc^{Fe}) in dry degassed benzene (1), $\text{Pc}^{\text{Fe}}\text{Py}_2$ in benzene with an admixture of pyridine (2) and $\text{HPc}^{\text{Fe}}\text{Cl}$ in benzene (3) ($c \approx 10^{-3}$ mol litre $^{-1}$, $l = 0.01$ cm).

The electronic absorption spectra of Pc^{Fe} in the gas phase and in noncoordinating solvents depend on the procedure for the preparation and the purity of the specimen. In our opinion, the most reliable data were obtained for sublimed specimens of Pc^{Fe} dissolved in naphthalene at 110 °C in an atmosphere of helium.⁵⁶ Bands similar in shape and position were observed in the electronic absorption spectra of benzene solutions of $\text{Pc}^{\text{R}}\text{Fe}$ under an inert atmosphere (Table 3, Fig. 1).^{6, 7} The spectra of $\text{Pc}^{\text{R}}\text{Fe}$ both in the gas phase⁶¹ and in noncoordinating solvents^{6, 7, 56} are untypical of the $\text{Pc}^{\text{R}}\text{M}$ complexes (M is metal).^{61, 62} For example, the electronic absorption spectra of iron(II) tetrakis(4-*tert*-butyl)phthalocyanine (Pc^{Fe}) always have several overlapping bands with approximately equal intensities in the long-wavelength region (580–750 nm), whereas this region in the spectrum of its bisaxially coordinated adduct $\text{Pc}^{\text{Fe}}\text{Py}_2$ is typical of the $\text{Pc}^{\text{R}}\text{M}$ complexes (Fig. 1). (It should be noted that axial coordination in the $\text{Pc}^{\text{R}}\text{M}$ complexes of other metals affects rather slightly the electronic absorption spectral patterns.) Originally, this anomaly was attributed to the fact that the $\text{Pc}^{\text{R}}\text{Fe}$ complexes are strongly aggregated in noncoordinating solvents.²⁹ However, more recent studies of $\text{Pc}^{\text{R}}\text{Fe}$ complexes containing bulky substituents at the α position of the phthalocyanine macrocycle did not confirm this suggestion. Thus the spectral patterns of both sterically unhindered complexes and complexes containing bulky substituents, which prevent intermolecular aggregation (for example, the 2,4,6-trimethylphenyl substituents), are approximately identical.⁷ In this connection and taking into account that the planar-square environment is untypical of iron(II) complexes, it was suggested⁷ that $\text{Pc}^{\text{R}}\text{Fe}$ complexes have a tetrahedrally distorted geometry, which leads to a change in the electronic absorption spectra.

The configuration of the ground electronic state of $\text{Pc}^{\text{R}}\text{Fe}$ has been discussed in the literature over a long period. In the late 1960s, based on the results of Mössbauer spectroscopy (including the data obtained in magnetic fields), Dale postulated that the ground electronic state of the iron ion in Pc^{Fe} has the $^3E_g[(d_{xy})^2(d_{xz}, d_{yz})^3(d_{z^2})^1]$ configuration.^{51, 63} Using the data on magnetic susceptibility of Pc^{Fe} , Lever⁵³ postulated another configuration of the iron ion, viz., $^3A_{2g}[(d_{xy})^2(d_{xz}, d_{yz})^2(d_{z^2})^2]$. Subsequent quantum-chemical calculations^{64, 65} and studies of the Mössbauer spectra of a wide range of substituted iron phthalocyanines^{27, 28} made it possible to state reliably that the ground electronic state of the iron ion in the compounds under study has the $^3E_g[(d_{xy})^2(d_{xz}, d_{yz})^3(d_{z^2})^1]$ configuration. Apparently, the sole exception is iron tetrakis(4-phenylthio)phthalocyanine, which has anomalous Mössbauer parameters (see Table 2). As a consequence, the configuration of the ground electronic state of

Table 3. Electronic absorption spectra of the $\text{Pc}^{\text{R}}\text{Fe}$ and $\text{TAP}^{\text{R}}\text{Fe}$ complexes in benzene.

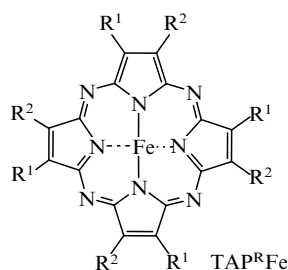
R^1	R^2	R^3	R^4	Positions of bands in electronic absorption spectra/nm ($10^{-5}\epsilon$)	Ref.
$\text{Pc}^{\text{R}}\text{Fe}$					
H	Bu ^t	H	H	690 sh, 647, 550, 350	6
2,4,6-Me ₃ C ₆ H ₂	H	H	H	690 sh, 647(0.60), 550(0.18), 460 sh, 410 sh, 352(0.46)	7
2,4,6-Me ₃ C ₆ H ₂	H	Bu ^t	H	710 sh, 653, 550, 490 sh, 450 sh, 354	7
H	Bu ⁱ	Bu ⁱ	H	710 sh, 660(0.72), 562(0.16), 470 sh, 420 sh, 345(0.55)	7
$\text{TAP}^{\text{R}}\text{Fe}$					
Et	Et			659 sh, 590, 561 sh, 537 sh, 489, 474 sh, 427, 339	57
Ph	Ph			626, 443, 330 (see ^a)	58
					
4-Bu ^t C ₆ H ₄	4-Bu ^t C ₆ H ₄			648(1), 550(0.34), 386(1.24), 322(1.93)	59
				635(4.41), 595(4.30), 455(4.38), 345(4.85)	60

^a The parameters of Mössbauer spectra at 300 K relative to metallic iron: $\delta = 0.05 \text{ mm s}^{-1}$, $\Delta E_Q = 2.53 \text{ mm s}^{-1}$.⁵⁸

the iron ion in this compound was described as $^3A_{2g}[(d_{xy})^2(d_{xz}, d_{yz})^2(d_{z^2})^2]$.²⁷

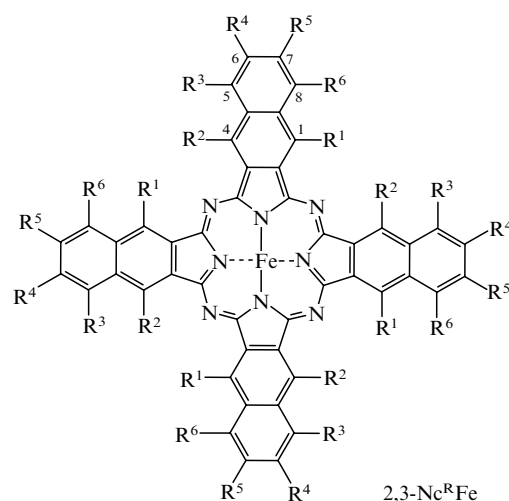
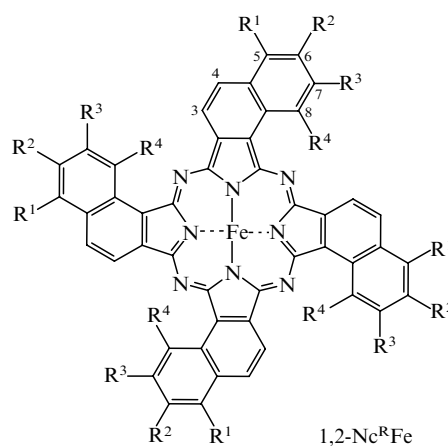
The reaction of PcFe with potassium *tert*-butylthiolate in the presence of 2,2,2-cryptand ($\text{C}\bar{\text{C}}222$) afforded the one-electron-reduced complex $[\text{C}\bar{\text{C}}222]^+[\text{PcFe}]^-$.⁴² The reaction of PcFe with LiAlH_4 and 18-crown-6 (18-C-6) in a THF solution yielded the two-electron-reduced complex $[\text{Li}_2(\text{THF})(18\text{-C-6})_2]^{2+}[\text{PcFe}]^{2-}$.⁴² In both cases, the central iron atom is coordinated by four nitrogen atoms of the isoindole fragments of the planar phthalocyanine ligand (see Table 1). Based on the results of spectral studies, the following two schemes of the equilibrium of isoelectronic forms of the one- and two-electron-reduced complexes were proposed: $[\text{Fe}^{\text{I}}\text{Pc}^{2-}] \rightleftharpoons [\text{Fe}^{\text{II}}\text{Pc}^{3-}]$ and $[\text{Fe}^{\text{I}}\text{Pc}^{3-}] \rightleftharpoons [\text{Fe}^{\text{II}}\text{Pc}^{4-}]$.

Complexes of iron tetraazaporphin ($\text{TAP}^{\text{R}}\text{Fe}$) have been poorly studied.^{6, 57–60, 66}



Presently, only octaphenyl-^{58, 60} octaethyl-⁵⁷ dibenzobarrelene-^{59, 66} and octakis(4-*tert*-butylphenyl)-containing⁶⁰ complexes (see Table 3 and notes therein) are reliably characterised by electronic absorption spectra, Mössbauer spectra and magnetic susceptibility data. On the basis of the data from magnetic susceptibility (3.8 ⁵⁸ and $3.82 \mu_B$ ⁵⁷ for octaphenyl- and octaethylporphyrzine iron complexes, respectively) and Mössbauer spectroscopy, all $\text{TAP}^{\text{R}}\text{Fe}$ complexes were assigned to iron(II) compounds characterised by the intermediate ($S = 1$) spin state.

Due to the low stability of iron 1,2-naphthalocyanine complexes (1,2-Nc^RFe) and, particularly, iron 2,3-naphthalocyanine complexes (2,3-Nc^RFe), which are prone to oxidation, reliable data on their properties in solutions are lacking. However, these complexes are stable in the solid state, which made it possible to measure their Mössbauer spectra. According to the available results, 2,3-NcFe belongs to iron(II) compounds with the intermediate ($S = 1$) spin.²⁷



Fused aza analogues of PcFe , viz., complexes of tetrakis(2,3-quinoxalino- and -quinolino)porphyrzines, were also synthesised and their thermal stabilities have been examined.⁶⁷

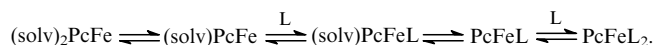
III. Bisaxially coordinated complexes of iron phthalocyanine and its analogues

1. Iron(II) complexes

Coordinatively unsaturated compounds $\text{Pc}^{\text{R}}\text{Fe}$ readily form axially coordinated diamagnetic low-spin ($S = 0$) complexes of

the general formula $\text{Pc}^{\text{R}}\text{FeL}_2$ with nitrogen-,^{15, 17, 46, 68–73} phosphorus-,⁷⁴ sulfur-⁴⁷ and carbon-containing^{75, 76} σ -donor and (or) π -acceptor ligands (L). In addition, mixed complexes with different axial ligands of the general formula $\text{Pc}^{\text{R}}\text{FeL}^1\text{L}^2$ can be formed.^{76–78}

The formation of bisaxially coordinated PcFeL_2 complexes, where L are nitrogen bases, was investigated in detail by kinetic methods.^{77–84} According to concepts developed in these studies, the stepwise successive coordination of two ligand molecules proceeds by a dissociation mechanism



Among complexes of the $\text{Pc}^{\text{R}}\text{FeL}_2$ type, compounds containing nitrogen bases of the heteroaromatic or aliphatic series as axial ligands were studied in most detail.^{46, 68, 69, 71, 72} Complexes with ligands containing the pyridine nitrogen atoms (which act simultaneously as σ -donors and π -acceptors) are more stable compared to complexes containing aliphatic amines (pure σ -donors).^{46, 71, 73} Stynes⁷⁸ studied the kinetics of replacement of the axial ligand in PcFeL_2 , where L is methylimidazole, pyridine or piperidine, by benzyl isocyanide. The direct replacement of one axial ligand was observed only in the dark. When illuminated in the presence of L, the resulting complex $\text{PcFeL}(\text{BnNC})$ reverted to PcFeL_2 .⁷⁸

Pyridine derivatives containing substituents at the β and γ positions enter into the reaction of axial coordination, whereas substituents at the α position inhibit this reaction.⁶⁹ Iron phthalocyanine also readily reacts with primary aliphatic amines, including such sterically hindered compounds as *tert*-butylamine.⁷¹ The range of dialkylamines, which can be axially coordinated to $\text{Pc}^{\text{R}}\text{Fe}$, is narrower. Branching of the carbon skeleton at the α -carbon atom [Pr_2^1NH , $(\text{cyclo-C}_6\text{H}_{11})_2\text{NH}$] prevents the preparation of axially coordinated complexes of the PcFeL_2 type.^{46, 71} In other words, as in the case of pyridine-type ligands, the choice of dialkylamines which can be axially coordinated is limited by steric factors. It is even more difficult to prepare axially coordinated complexes of this type with trialkylamines. Thus an unstable complex with quinuclidine is the only compound of this type, which was isolated and characterised by spectroscopic methods.⁷²

Unlike tertiary amines, trisubstituted phosphines and phosphites readily form complexes with PcFe .^{74, 85, 86} Compounds of the $\text{Pc}^{\text{R}}\text{FeL}_2$ type, where L are aliphatic or aromatic isocyanides,⁷⁵ carbon monoxide^{47, 76–78} or the cyanide ion,^{68, 87, 88} are also well studied. Of complexes containing the Fe—S bond, only those with tetrahydrothiophene and DMSO have been described.^{43, 47} Data on analogous complexes containing the Fe—O bonds are lacking in the literature. Among mixed-ligand complexes of the $\text{Pc}^{\text{R}}\text{FeL}^1\text{L}^2$ type, compounds $\text{PcFe}(\text{CO})\text{L}$ (where L is nitrogen-, sulfur- or oxygen-containing ligands),^{47, 76, 78, 87} $\text{Pc}^{\text{R}}\text{Fe}(\text{CN})\text{L}$ (where L is a nitrogen-containing ligand)⁵⁰ and PcFeL^1L^2 (where L^1 and L^2 are either two different nitrogen-containing ligands⁷⁷ or isocyanide and nitrogen-containing ligands⁷⁸) were studied.

The structures of several complexes of the PcFeL_2 type, viz., $\text{PcFe}(\text{4-MeC}_5\text{H}_4\text{N})_2$, $\text{PcFe}(\text{MeIm})_2$, $\text{PcFe}(\text{DMSO})_2$, $\text{PcFe}(\text{4-MeC}_5\text{H}_{10}\text{N})_2$ and $\text{PcFe}(\text{CO})(\text{DMF})$, were established by X-ray diffraction analysis (see Table 1).^{43–47} It should be noted that the axial ligands in $\text{PcFe}(\text{4-MeC}_5\text{H}_4\text{N})_2$ and $\text{PcFe}(\text{MeIm})_2$ are located in two mutually perpendicular planes, whereas these ligands in $\text{PcFe}(\text{4-MeC}_5\text{H}_{10}\text{N})_2$ are virtually coplanar. This suggests a substantial contribution of back π -bonding in the $\text{PcFe}(\text{4-MeC}_5\text{H}_4\text{N})_2$ and $\text{PcFe}(\text{MeIm})_2$ complexes. For the same reason, the Fe—CO distance in the $\text{PcFe}(\text{CO})(\text{DMF})$ complex is shorter than the corresponding distances in the complexes with other axial ligands and shorter than the Fe—N(Pc) distance (see Table 1). Analogous effects were also observed in complexes with strong π -acceptors, such as isocyanide ligands (see Table 1).^{48, 49}

The electronic absorption spectra of PcFeL_2 containing axial ligands of virtually all known types were measured.^{46, 62, 68–74, 77–84, 87} These spectra consist of a long-wave-

length Q band at 660 nm which has vibrational structure, a charge-transfer band (CTB) at 425 nm and a B band at 330 nm. The σ - and π -acceptor properties of the axially coordinated ligands in these complexes most substantially affect the positions of the charge-transfer bands (Table 4).^{68, 69, 71, 87} The above-mentioned effect has been examined many times (see, for example, Refs 46, 68, 69 and 71). Based on the results of calculations by the extended Hückel method, Goutermann and coworkers⁶⁴ were the first to assign this band to charge transfer from the central iron ion to the unoccupied orbital of the axial ligand (CTB $\text{Fe} \rightarrow \text{L}$). More recently, Dale⁶⁸ studied a series of PcFeL_2 complexes, where L is pyridine, imidazole, butylamine, piperidine, ammonia or the cyanide ion, and assigned this band to $\text{Fe} \rightarrow \text{Pc}$ charge transfer and related its position to the basicity of the axial ligand. Analogous correlations were also observed for a wide range of pyridine⁶⁹ and alkylamine⁷¹ ligands. Ouedraogo and coworkers⁶⁹ followed Goutermann in attributing this band to $\text{Fe} \rightarrow \text{L}$ charge transfer. However, Stillman and coworkers⁸⁷ examined electronic absorption spectra as well as magnetic circular dichroism spectra of a series of PcFeL_2 complexes and demonstrated that the above-mentioned band belongs to a transfer in which one of the states is degenerate. The transition from the $3d_\pi$ orbitals of the central iron atom with symmetry e_g to the unoccupied π^* orbital of the phthalocyanine ligand with the symmetry b_{1u} is the only allowed transition for the low-spin d^6 configuration of the $\text{Fe}(\text{II})$ ion in a complex with D_{4h} symmetry. The axial coordination of the purely σ -donor ligands, for example, of alkylamines, occurs primarily owing to the interaction between the d_{z^2} orbital of the central atom and the n orbital of the ligand. The enhancement of the σ -donor character of the axial ligand leads to an increase in the population of the d_{z^2} orbital of the iron atom and, consequently, to its destabilisation as well as to destabilisation of the d_π orbitals, which, in turn, leads to a bathochromic shift of the charge-transfer band.^{71, 87} The enhancement of the π -acceptor character of the axial ligands results in direct stabilisation of the d_π orbitals of the central atom and, as a consequence, in an increase in the energy of the charge-transfer band. Thus this band is observed at 450, 430, 415 and 400 nm for the PcFeL_2 complexes with the cyanide (σ - and π -donors),^{87, 88} alkylamine (pure σ -donors),^{46, 68, 71} pyridine (σ -donors and π -acceptors)^{68, 69, 87, 90} and isocyanide (weak σ -donors and strong π -acceptors)^{75, 76, 78} ligands, respectively, (see Table 4). To obtain an adequate correlation between the basicity of the axial ligands and the position of the charge-transfer band, the steric properties of these ligands should also be taken into account.⁷¹ A new approach to the estimation of the positions of charge-transfer bands in the spectra of the PcFeL^1L^2 complexes with ligands of all types on the basis of their electronic structures and steric properties using second-order perturbation theory was proposed.^{46, 92} The electronic absorption spectra of the PcFeL_2 complexes with axial pyridine-type ligands containing acceptor substituents have an additional band at 500 nm. This band was assigned to $\text{Fe} \rightarrow \text{L}$ charge transfer.⁶⁹ It should be noted that the nature of the solvent has differing effects on the position of the charge-transfer band in $\text{Pc}^{\text{R}}\text{FeL}_2$ complexes depending on the type of axial ligand. Thus if the axial ligands can form a dative π bond (pyridine-type ligands, isocyanides, etc.), the position of the charge-transfer band depends only slightly on the nature of the solvent. For example, the charge-transfer band for the PcFePy_2 complex was observed at 415, 413.5 and 412 nm in DMSO, pyridine and dichloromethane, respectively.^{68, 69, 79, 87} In the case of alkylamines and, particularly, polyamines, which can form an intramolecular hydrogen bond, the position of this band varies over a wide range depending on the nature of the solvent.^{68, 69, 71, 87} For example, the charge-transfer band for the $\text{PcFe}(\text{NH}_3)_2$ complex is observed at 440 and 426 nm in DMSO⁶⁸ and dichloromethane,⁸⁷ respectively. Probably, this behaviour reflects a decrease in the bond energy on going to the $\text{Pc}^{\text{R}}\text{FeL}_2$ complexes with pure σ -donor ligands. However, there is no direct evidence for this suggestion.

Table 4. Electronic absorption spectra of PcFeL₂ complexes.

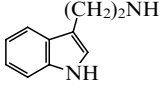
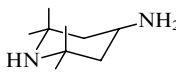
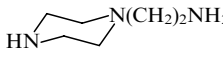
L	Solvent	Positions of bands in electronic absorption spectra/nm (log ε)	Relative intensity	Ref.
NH ₃	PhH – L	664, 637, 604, 425, 335	2.08 : 0.72 : 0.61 : 0.3 : 1	71
MeNH ₂	PhH – L	664, 637, 603, 427.5, 335	2.05 : 0.56 : 0.47 : 0.31 : 1	71
Pr ⁿ NH ₂	PhH – L	664, 637, 605, 427.5, 334	1.47 : 0.81 : 0.57 : 0.28 : 1	71
Pr ⁱ NH ₂	PhH – L	663, 636, 604, 424.5, 334	1.64 : 0.7 : 0.64 : 0.28 : 1	71
Bu ⁿ NH ₂	PhH – L	664, 637, 605, 427, 334	1.58 : 0.71 : 0.6 : 0.35 : 1	71
Bu ^s NH ₂	PhH – L	663, 636, 604, 425, 334	2.06 : 0.8 : 0.69 : 0.32 : 1	71
Bu ^t NH ₂	PhH – L	663, 635, 606, 427, 332	1.37 : 0.61 : 0.52 : 0.25 : 1	71
Bu ⁱ NH ₂	PhH – L	661, 634, 600, 421.5, 331	2.23 : 0.68 : 0.57 : 0.32 : 1	71
n-C ₅ H ₁₁ NH ₂	PhH – L	665, 636, 606, 428, 331	1.45 : 0.55 : 0.47 : 0.24 : 1	71
n-C ₆ H ₁₃ NH ₂	PhH – L	663, 636, 604, 427.5, 333	1.75 : 0.72 : 0.51 : 0.21 : 1	71
(EtO) ₃ Si(CH ₂) ₃ NH ₂	PhH – L	664, 637, 605, 428, 334	1.65 : 0.64 : 0.55 : 0.29 : 1	71
CF ₃ CH ₂ NH ₂	PhH – L	655, 628, 595, 416, 330	1.82 : 0.6 : 0.52 : 0.29 : 1	71
cyclo-C ₆ H ₁₁ NH ₂	PhH – L	663, 636, 603, 425, 332	1.61 : 0.56 : 0.49 : 0.33 : 1	71
BnCH(NH ₂)Me	PhH – L	662, 635, 602, 425, 335	1.48 : 0.57 : 0.48 : 0.27 : 1	71
	PhH – L	664, 637, 604, 427.5, 333	1.70 : 0.52 : 0.46 : 0.29 : 1	71
Ph(CH ₂) ₂ NH ₂	PhH – L	664, 635, 603, 426.5, 333	—	71
BnNH ₂	PhH – L	663, 636, 604, 424, 334	1.45 : 0.65 : 0.55 : 0.29 : 1	71
	PhH – L	664, 637, 604, 426.5, 330	1.50 : 0.57 : 0.49 : 0.24 : 1	71
	PhH – L	665, 640, 607, 430, 334	1.44 : 0.66 : 0.58 : 0.29 : 1	71
cyclo-(C ₆ H ₁₀)(NH ₂) ₂	PhH – L	666, 639, 605, 432, 335	2.39 : 0.74 : 0.63 : 0.36 : 1	71
NH ₂ (CH ₂) ₂ NH ₂	CH ₂ Cl ₂	667, 640, 606, 435, 330	—	89
NH ₂ (CH ₂) ₃ NH ₂	PhH – L	665, 639, 607, 433, 334	1.72 : 0.75 : 0.69 : 0.32 : 1	71
NH ₂ (CH ₂) ₄ NH ₂	PhH – L	666, 640, 608, 433, 334	1.84 : 0.81 : 0.71 : 0.35 : 1	71
NH ₂ (CH ₂) ₅ NH ₂	PhH – L	665, 636, 604, 429, 337	2.51 : 0.78 : 0.66 : 0.37 : 1	71
NH ₂ (CH ₂) ₇ NH ₂	PhH – L	664, 636, 603, 428, 334	3.41 : 1 : 0.87 : 0.43 : 1	71
HO(CH ₂) ₂ NH(CH ₂) ₃ NH ₂	PhH – L	670, 640, 608, 437, 338	1.88 : 0.67 : 0.6 : 0.45 : 1	71
Pip	PhH – L	663, 636, 605, 426.5, 334	2.01 : 0.71 : 0.65 : 0.29 : 1	71
	DMSO – L	663, 642, 602, 434	—	69
	CH ₂ Cl ₂	659, 598, 425, 340	—	87
4-MeC ₅ H ₁₀ N	PhH – L	662, 635, 602, 427, 335	2.02 : 0.61 : 0.51 : 0.35 : 1	71
Mor	PhH – L	660, 633, 601, 423, 332	2.05 : 0.82 : 0.66 : 0.28 : 1	71
Et ₂ NH	PhH – L	662, 637, 602, 426, 333	1.61 : 0.53 : 0.45 : 0.32 : 1	71
Pr ₂ NH	PhH – L	663, 637, 603, 426.5, 334	1.61 : 0.52 : 0.44 : 0.28 : 1	71
Py	DMSO – L	655(5.07), 593(4.47), 413(4.32), 332(4.82)	—	79
	CH ₂ Cl ₂	651, 591, 412, 328	—	68
3-MeC ₅ H ₄ N	CHCl ₃	655, 630, 595, 415	—	69
4-MeC ₅ H ₄ N	CHCl ₃	656, 630, 595, 412.5	—	69
	CHCl ₃	656, 594, 410, 328	—	90
	CH ₂ Cl ₂	652, 592, 413, 331	—	87
3,4-Me ₂ C ₅ H ₃ N	CHCl ₃	656, 630, 595, 412.5	—	69
3,5-Me ₂ C ₅ H ₃ N	CHCl ₃	656, 630, 595, 415	—	69
3-OHC ₅ H ₄ N	DMSO	656, 630, 595, 412	—	69
4-OHC ₅ H ₄ N	DMSO	662, 635, 602, 432	—	69
3-ClC ₅ H ₄ N	CHCl ₃	653, 627, 592, 446, 407	—	69
4-ClC ₅ H ₄ N	DMSO	680, 642, 613, 555	—	69
3,5-Cl ₂ C ₅ H ₃ N	CHCl ₃	650, 625, 591, 465, 397	—	69
3-CHOC ₅ H ₄ N	DMSO	655, 630, 595, 410	—	69
4-CHOC ₅ H ₄ N	DMSO	654, 630, 595, 520 sh, 410	—	69
3-CNC ₅ H ₄ N	CHCl ₃	651, 625, 591, 482, 402	—	69
4-CNC ₅ H ₄ N	CHCl ₃	652.5, 625, 591, 527 sh, 405	—	69
Im	CHCl ₃	663, 640, 602, 430	—	69
	CH ₂ Cl ₂	657, 596, 423, 339	—	87
MeIm	CH ₂ Cl ₂	658, 597, 423, 338	—	87
	PhH – L	659, 632, 597, 423.5, 340	2.89 : 0.8 : 0.69 : 0.34 : 1	76
	PhH – L	655, 594, 408, 335	1.48 : 0.38 : 0.27 : 1	76

Table 4 (continued).

L	Solvent	Positions of bands in electronic absorption spectra/nm (log ϵ)	Relative intensity	Ref.
	PhH–L	654, 595, 412, 327	1.71 : 0.45 : 0.23 : 1	76
CN [−]	CH ₂ Cl ₂	664, 602, 426, 394, 310	—	87
CN [−] /N ₂ H ₄	CH ₂ Cl ₂ –N ₂ H ₄	663, 635, 600, 425, 357, 310	—	50
NH ₃ /CO	CH ₂ Cl ₂	659, 596, 363, 317, 288	—	87
N ₂ H ₄	CH ₂ Cl ₂ –N ₂ H ₄	660, 633, 597, 417, 327	—	50
Bu ^t NC	CHCl ₃	658, 598, 387 sh, 326	—	91
cyclo-C ₆ H ₁₁ NC	CHCl ₃	658, 598, 386 sh, 325	—	91
PhNC	CHCl ₃	658, 598, 325	—	91
Me ₂ C ₆ H ₃ NC	CHCl ₃	658, 598, 393 sh, 325	—	91
<i>o</i> -MeC ₆ H ₄ NC	CHCl ₃	663, 601, 388 sh, 319	—	91
<i>m</i> -MeC ₆ H ₄ NC	CHCl ₃	662, 598, 391, 324	—	91
<i>p</i> -MeC ₆ H ₄ NC	CHCl ₃	663, 599, 392, 324	—	91
Pr ⁱ C ₆ H ₄ NC	CHCl ₃	662, 598, 391, 325	—	91

Note. Pip is piperidine, Mor is morpholine and Im is imidazole.

In some cases, the position of the charge-transfer band can be used for analytical purposes, for example, for the determination of CO concentration. Thus when CO was bubbled through a solution of PcFePy₂, the intensity of the charge-transfer band decreased as the amount of the resulting PcFe(CO)Py complex increased.⁷⁸ Analogously, in the reaction of the PcFePy₂ complex with isocyanides, the intensity of the band of the initial complex (at 420 nm) first decreased [the formation of PcFePy(NCR), which gave weak bands at 420 and 394 nm] and then disappeared [the formation of PcFe(NCR)₂, which gave a charge-transfer band at 394 nm].

The Mössbauer spectra of polycrystalline samples or frozen solutions of the PcFeL¹L² complexes were examined (Table 5).^{9, 46, 47, 69, 71, 76, 86, 93–98} The spectra of freshly prepared samples of PcFeL¹L² are manifested as doublets and their parameters are characteristic of low-spin ($S = 0$) iron(II) complexes.^{99, 100} The δ values vary rather slightly, whereas the ΔE_Q value varies over a wider range depending on the nature of the ligand (see Table 5). The isomer shift reflects the s -electron density at the iron nucleus.⁹⁹ Consequently, an increase in the population of the $4s$ orbital of the iron atom leads to a decrease in the δ value. For the complexes under consideration, an increase in the population of the $4s$ orbital of the central atom results directly from an increase in the σ -donor character of the axial ligand and from the fact that the $3d_{z^2}$ and $4s$ orbitals of the central iron atom have the same symmetry and can be mixed.⁹⁹ The ΔE_Q value, which characterises the electric field gradient about the iron nucleus, is more sensitive to the structure of the axial ligand (see Table 5).⁹⁹

$$\Delta E_Q = 1/2eQV_{zz}(1 + 1/3\eta^2)^{1/2}, \quad (1)$$

where $V_{zz} = eq$, $\eta = (|V_{xx} - V_{yy}|)/|V_{zz}|$.

For the PcFeL₂ complexes, $V_{xx} \approx V_{yy}$, and, consequently, $\eta \approx 0$.^{76, 95, 101} The electric field gradient has a positive sign.^{95, 101} For the low-spin iron(II) complexes, the q parameter can be represented as the sum $q = q_{\text{lat}} + q_{\text{val}} + q_{\text{mo}}$.^{99, 102, 103} The first member q_{lat} corresponds to the lattice contribution to the electric field gradient. This value decreases proportionally to the cube of the distance and is negligibly small for bulky complexes. The third member q_{mo} is associated with the difference in the population of different MOs belonging to the same irreducible representation. For the low-spin iron(II) complexes, the ground electronic state has the $(d_{xy})^2(d_{xz}, d_{yz})$ configuration,⁴ and, consequently, this term is equal to zero. The term q_{val} reflects the symmetry of the population of the atomic orbitals of the iron atom and its σ and π interactions with the ligands. This term can be written as follows^{99, 103}

$$q_{\text{val}} = 4/7(1 - R) < r^{-3} >_{3d} [n_{x^2-y^2} + n_{xy} - n_{z^2} - 1/2(n_{xz} + n_{yz})],$$

where R is the Sternheimer factor for antishielding of the iron nucleus, $< r^{-3} >_{3d}$ is the radial component of the $3d$ wave function and n is the population of the corresponding AO.

If the coordination environment about the iron atom is nearly octahedral, the q_{val} term for the low-spin t_{2g} configuration is equal to zero.^{99, 103} In the case of axial distortion, the q_{val} term makes the major contribution to the electric field gradient in complexes of the Pc^RFeL₂ type. Actually, the quadrupole splitting in nearly octahedral complexes with isocyanide ligands is small,^{9, 90} whereas this splitting in complexes with nitrogen-centred axial ligands is significant (see Table 5).^{46, 68, 69, 71, 93, 95–97} An increase in the ΔE_Q value is observed in the following series of axial ligands: isocyanides $\approx$ cyanides $<$ CO $<$ phosphites $<$ (CO)L $\approx$ phosphines $<$ pyridines, alkylamines and other nitrogen-containing ligands. Analysis of Eqn (1) demonstrates that the quadrupole splitting should decrease as both the σ -donor and π -acceptor properties of the axial ligands are strengthened. However, the observed ΔE_Q values for some complexes with ligands exhibiting pronounced π -acceptor properties (CO or isocyanides) are higher than the expected values (see Table 5).^{47, 76} To account for this anomalous behaviour, hypotheses for the *cis* and *trans* effects of the axial ligands on the phthalocyanine macrocycle were invoked.⁷⁶ However, the mechanism that causes a decrease in the quadrupole splitting is still an open question.

Attempts were also made to interpret the available results with the use of empirical and semiempirical approaches. Thus a simple empirical procedure was proposed for the estimation of the ΔE_Q value for the PcFeL₂ complexes using absolute partial quadrupole splittings.¹⁰⁴ A reasonable correlation between the ΔE_Q values and the basicity was obtained.^{46, 92} A correlation between the ΔE_Q values and the steric properties of alkylamines was also found.⁷¹ An approach based on perturbation theory was also proposed for the estimation of the ΔE_Q values for all types of axial ligands.^{46, 92}

The effect of circulating currents of the extended π system on the chemical shifts is clearly manifested in the ¹H NMR spectra of the Pc^RFeL₂ complexes. In all cases, the signals of the coordinated ligands are shifted upfield compared to the signals of the initial amines (Table 6).^{72, 90, 105–109} The high selectivity of axial coordination, high induced shifts of the proton signals and the possibility of the prediction of their positions on the basis of the results of quantum-chemical calculations allow one to solve successfully a number of analytical problems.^{105–108}

Table 5. Parameters of Mössbauer spectra of the PcFeL^1L^2 complexes.

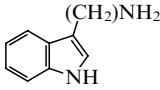
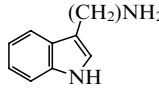
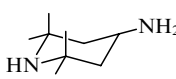
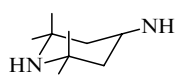
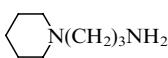
L^1	L^2	T/K	$\delta^a/\text{mm s}^{-1}$	$\Delta E_Q/\text{mm s}^{-1}$	Ref.
Pr^nNH_2	Pr^nNH_2	300	0.50	1.97	97
Pr^iNH_2	Pr^iNH_2	298	0.51	2.02	71
Bu^nNH_2	Bu^nNH_2	77	0.34 ^b	1.94	93
Bu^sNH_2	Bu^sNH_2	298	0.52	1.97	71
Bu^tNH_2	Bu^tNH_2	298	0.61	2.38	71
$\text{CF}_3\text{CH}_2\text{NH}_2$	$\text{CF}_3\text{CH}_2\text{NH}_2$	298	0.62	2.49	71
		298	0.48	1.95	71
		298	0.51	1.96	71
		298	0.46	1.76	71
$\text{NH}_2(\text{CH}_2)_4\text{NH}_2$	$\text{NH}_2(\text{CH}_2)_4\text{NH}_2$	298	0.48	1.84	71
Mor	Mor	298	0.53	2.31	71
Et_2NH	Et_2NH	300	0.51	2.22	97
Pip	Pip	298	0.52	2.20	71
		77	0.364 ^b	2.19	69
		77	0.33 ^b	2.21	93
		295	0.28 ^b	2.34	95
		115	0.36 ^b	2.25	
		4.2	0.34 ^b	2.24	
4-MeC ₅ H ₁₀ N MeIm	4-MeC ₅ H ₁₀ N MeIm	300	0.52	2.22	98
		298	0.53	2.27	71
		298	0.48	1.71	71
		298	0.51	1.79	73
		77	0.57	1.76	
		298	0.53	1.94	73
		298	0.51	1.73	73
Im	Im	77	0.55	1.68	
		77	0.313 ^b	1.74	69
		77	0.29 ^b	1.75	93
		295	0.54	1.79	96
		195	0.59	1.76	
Py	Py	77	0.63	1.71	
		77	0.322 ^b	1.94	69
		293	0.26 ^b	2.02	93
		77	0.33 ^b	1.97	
		300	0.53	2.01	98
3-MeC ₅ H ₄ N	3-MeC ₅ H ₄ N	295	0.53	2.05	96
		195	0.58	2.00	
		77	0.62	1.89	
		77	0.321 ^b	1.87	69
		295	0.55	1.95	96
4-MeC ₅ H ₄ N	4-MeC ₅ H ₄ N	195	0.60	1.88	
		77	0.61	1.81	
		77	0.347 ^b	1.97	69
		295	0.55	1.96	96
		195	0.58	1.89	
3,4-Me ₂ C ₅ H ₃ N	3,4-Me ₂ C ₅ H ₃ N	77	0.342 ^b	1.98	69
3,5-Me ₂ C ₅ H ₃ N	3,5-Me ₂ C ₅ H ₃ N	77	0.338 ^b	1.95	69
3-OHC ₅ H ₄ N	3-OHC ₅ H ₄ N	77	0.355 ^b	1.90	69
4-OHC ₅ H ₄ N	4-OHC ₅ H ₄ N	77	0.265 ^b	1.80	69
3-ClC ₅ H ₄ N	3-ClC ₅ H ₄ N	77	0.343 ^b	1.91	69
4-ClC ₅ H ₄ N	4-ClC ₅ H ₄ N	77	0.389 ^b	2.45	69
3,5-Cl ₂ C ₅ H ₃ N	3,5-Cl ₂ C ₅ H ₃ N	77	0.360 ^b	2.05	69

Table 5 (continued).

L ¹	L ²	T/K	δ^a /mm s ⁻¹	ΔE_Q /mm s ⁻¹	Ref.
3-CHOC ₅ H ₄ N	3-CHOC ₅ H ₄ N	77	0.345 ^b	1.97	69
4-CHOC ₅ H ₄ N	4-CHOC ₅ H ₄ N	77	0.325 ^b	1.84	69
3-CNC ₅ H ₄ N	3-CNC ₅ H ₄ N	77	0.355 ^b	2.17	69
4-CNC ₅ H ₄ N	4-CNC ₅ H ₄ N	77	0.340 ^b	1.90	69
Pyz	Pyz	298	0.5	2.006	9
MeC ₄ H ₃ N ₂	MeC ₄ H ₃ N ₂	298	0.498	1.895	9
2,3-Me ₂ C ₄ H ₂ N ₂	2,3-Me ₂ C ₄ H ₂ N ₂	298	0.498	1.968	9
ClC ₄ H ₃ N ₂	ClC ₄ H ₃ N ₂	298	0.513	2.149	9
EtC ₄ H ₃ N ₂	EtC ₄ H ₃ N ₂	298	0.504	2.016	9
		298	0.15 ^b	1.79	9
		298	0.53	2.20	47
DMSO	DMSO	298	0.50	2.08	47
PEt ₃	PEt ₃	291	0.16 ^b	1.54	86
		78.6	0.25 ^b	1.47	
PBu ₃	PBu ₃	291	0.15 ^b	1.57	86
		78.8	0.24 ^b	1.47	
		4.3	0.23 ^b	1.45	
P(OEt) ₃	P(OEt) ₃	291	0.13 ^b	1.07	86
		78.8	0.17 ^b	0.99	
		4.3	0.18 ^b	0.95	
P(OBu) ₃	P(OBu) ₃	298	0.42	1.05	86
		77	0.48	0.96	
CO	THF	298	0.36	1.82	76
CO	H ₂ O	298	0.37	1.75	76
CO	OPPh ₃	298	0.36	1.69	76
CO	HMPT	298	0.36	1.60	76
CO	DMSO	298	0.36	1.56	76
CO	DMF	298	0.35	1.56	76
CO	MeOH	298	0.37	1.56	76
CO		298	0.38	1.55	76
CO	Et ₂ NH	298	0.35	1.45	76
CO	Pip	298	0.37	1.27	76
CO	Py	298	0.37	1.19	76
CO	Pr ⁿ NH ₂	298	0.36	1.11	76
CO	NH ₃	298	0.38	1.02	76
CO	CO	298	0.36	0.82	76
CN	CN	77	0.19 ^b	0.56	93
Bu ^t NC	Bu ^t NC	298	0.16 ^b	0.79	9
cyclo-C ₆ H ₁₁ NC	cyclo-C ₆ H ₁₁ NC	298	0.13 ^b	0.69	9
PhNC	PhNC	298	0.11 ^b	0.67	9
Me ₂ C ₆ H ₃ NC	Me ₂ C ₆ H ₃ NC	298	0.12 ^b	0.70	9
Cl ₄ C ₆ HNC	Cl ₄ C ₆ HNC	298	0.09 ^b	0.67	9
Me ₂ C ₆ H ₂ (NC) _{2-1,4}	Me ₂ C ₆ H ₂ (NC) _{2-1,4}	298	0.11 ^b	0.65	9
C ₆ Me ₄ (NC) _{2-1,4}	C ₆ Me ₄ (NC) _{2-1,4}	298	0.12 ^b	0.66	9

Note. Pyz is , HMPT is hexamethylphosphotriamide; ^a relative to sodium nitroprusside; ^b relative to metallic iron.

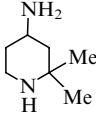
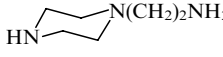
Studies of the thermal stability of a number of the Pc^RFePy₂ complexes demonstrated that both ligand molecules are eliminated in one stage. Electron-withdrawing substituents in the macrocycle increase thermal stability, whereas electron-donating substituents decrease this stability compared to that of the unsubstituted analogue.⁷⁰

Among axially coordinated PcFe(II) complexes, polymeric compounds of the general formula (Pc^RFeL)_n belong to a special group.^{9, 13, 109–113} These compounds attract great interest because of their semiconducting properties.^{114–119} Since several comprehensive reviews devoted to this subject are available,^{9, 13, 110, 112}

we restrict ourselves to consideration of the major representatives of this group.

Polymeric complexes (Pc^RFeL)_n were synthesised by the reactions of Pc^RFe with different bidentate ligands, such as pyrazine, tetrazine, 4,4'-dipyridyl, 1,4-diisocyanobenzene, 4-phenylenediamine and 9,10-anthracenediisocyanide, which serve as cross-linking agents. These complexes can be divided into two groups according to their semiconducting properties. The first group involves complexes exhibiting good semiconducting properties only upon doping with halogens or other electron acceptors. The second group consists of complexes exhibiting semiconduct-

Table 6. Parameters of ^1H NMR spectra of the axially coordinated ligands in the PcFeL_2 complexes.

L	Solvent	Positions of signals for protons of the coordinated ligand			Ref.
		NH_n	$\alpha\text{-CH}_n$	$\beta\text{-CH}_n$	
MeNH_2	CD_2Cl_2	−7.28	−2.73		108
	CDCl_3	−7.28	−2.73		106
	C_6D_6	−8.75	−3.70		107
Pr^iNH_2	CD_2Cl_2	−7.46	−3.09	−1.94	108
	CDCl_3	−7.67	−3.15	−1.94	73
Bu^sNH_2	CD_2Cl_2	−7.36	−3.49	−2.06	108
	CDCl_3	−7.78	−3.49	−2.06	73
Bu^nNH_2	CD_2Cl_2	−7.28	−2.98	−1.41	108
	CDCl_3	−7.44	−3.01	−1.41	73
Bu^iNH_2	CD_2Cl_2	−7.29	−3.21	−1.31	108
	CDCl_3	−7.45	−3.26	−1.16	73
$n\text{-C}_5\text{H}_{11}\text{NH}_2$	CD_2Cl_2	−7.17	−3.01	−1.42	108
$n\text{-C}_6\text{H}_{13}\text{NH}_2$	CD_2Cl_2	−7.17	−3.00	−1.41	108
	CDCl_3	−7.42	−3.00	−1.42	106
$\text{Bu}^n\text{CH}(\text{Et})\text{CH}_2\text{NH}_2$	CD_2Cl_2	−7.38	−3.01	−1.49	108
$(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NH}_2$	CD_2Cl_2	−7.18	−2.98	−1.26	108
	CD_2Cl_2	−7.48	−3.23	−2.23	108
Pip	CD_2Cl_2	−7.89	−3.12	−1.46	108
Et_2NH	CD_2Cl_2	−7.97	−3.12	−1.80	108
$\text{NH}_2(\text{CH}_2)_3\text{NH}_2$	CD_2Cl_2	−6.43	−2.86	−1.24	108
$\text{NH}_2(\text{CH}_2)_4\text{NH}_2$	CD_2Cl_2	−6.46	−3.01	−1.31	108
	CDCl_3	−6.58	−3.05	−1.4	105
$\text{NH}_2(\text{CH}_2)_5\text{NH}_2$	CD_2Cl_2	−7.06	−3.00	−1.39	108
$\text{NH}_2(\text{CH}_2)_7\text{NH}_2$	CD_2Cl_2	−7.15	−3.09	−1.43	108
	CD_2Cl_2	−6.65	−2.86	−0.70	108
	CDCl_3	−6.81	−2.80	−0.3	108
	C_6D_6	−7.10	−3.22	−1.18	108
	CDCl_3	−6.18	−2.9	−0.98	108
$\text{HO}(\text{CH}_2)_2\text{NH}_2$	CD_2Cl_2	−6.85	−2.95	−2.14	108
$\text{HO}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_2\text{NH}_2$	CD_2Cl_2	−6.06	−2.74	−1.18	108
$4\text{-MeC}_5\text{H}_4\text{N}$	CDCl_3		1.95	4.78	90
Pyz	CDCl_3		1.92	6.01	90

ing properties without doping (Table 7). Polymeric compounds of the first type are stable up to 100–130 °C and lose their semi-conducting properties in the absence of the doping agent. All complexes except for compounds containing tetrazine as the axial ligand belong to this type. Tetrazine-containing polymers belong to the second type. The latter are thermally more stable and have no need of doping.^{9, 13, 110, 112}

Of the axially coordinated $\text{TAP}^{\text{R}}\text{FeL}_2$ complexes reported in the literature, only complexes of iron octaphenylporphyrazine, where L is a pyridine-type ligand, alkylamine or the cyanide ion, were systematically studied by electronic and Mössbauer spectroscopy (Table 8).^{58, 120–122} All complexes of this type belong to low-spin iron(II) compounds. The δ and ΔE_Q values (relative to sodium nitroprusside) were determined for some octaphenyl-substituted complexes:

Complex	$\delta/\text{mm s}^{-1}$	$\Delta E_Q/\text{mm s}^{-1}$	Ref.
$\text{TAP}^{\text{Ph}}\text{FePy}_2$	0.47	2.26	58
$\text{TAP}^{\text{Ph}}\text{Fe}(4\text{-MeC}_5\text{H}_4\text{N})_2$	0.45	2.30	58
$\text{TAP}^{\text{Ph}}\text{FeIm}_2$	0.18	2.12	58
	0.50	2.10	120, 121

The electronic absorption spectra of the octaphenyl-substituted $\text{TAP}^{\text{Ph}}\text{FeL}_2$ complexes with pyridine-type ligands are analogous in general appearance to those of the PcFeL_2 complexes (Fig. 2).^{6, 57, 58} The band at 550 nm was attributed to the

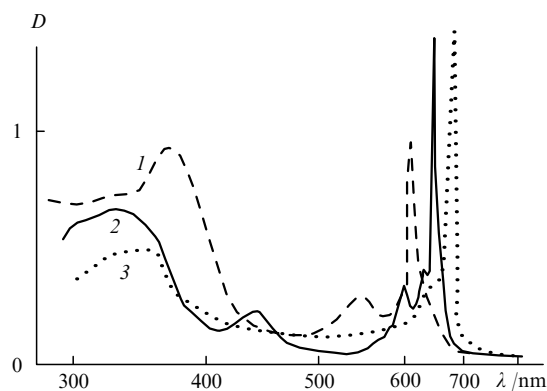
**Figure 2.** Electronic absorption spectra of the complexes $\text{TAP}^{\text{Ph}}\text{FePy}_2$ (1), PcFePy_2 (2) and $2,3\text{-NcFePy}_2$ (3) in benzene.

Table 7. Selected characteristics of the polymeric complexes of iron phthalocyanines ($\text{Pc}^{\text{R}}\text{FeL}$)_n and iron naphthalocyanines ($\text{Nc}^{\text{R}}\text{FeL}$)_n.^{9, 13, 110–114}

R ¹	R ²	R ³	R ⁴	L	σ /S cm ⁻¹	T/K	δ^{a} /mm s ⁻¹	ΔE_{Q} /mm s ⁻¹	Other characteristics ^b
Phthalocyanines									
H	H	H	H	C ₆ H ₄ (NC) ₂ -1,4	2×10^{-5}	293	0.12	0.68	ν_{NC} 2100
n-C ₇ H ₁₅	H	H	H	C ₆ H ₄ (NC) ₂ -1,4	2×10^{-10}	82	0.18	0.57	λ_{max} 671, 607, 394, 321; ν_{NC} 2095
H	n-C ₅ H ₁₁	H	H	C ₆ H ₄ (NC) ₂ -1,4	2×10^{-6}	82	0.18	0.48	λ_{max} 679, 610, 466, 395, 342, 303; ν_{NC} 2098
H	n-C ₇ H ₁₅	n-C ₇ H ₁₅	H	C ₆ H ₄ (NC) ₂ -1,4	4×10^{-9}	82	0.18	0.45	λ_{max} 680, 612 sh, 459, 331, 302; ν_{NC} 2100
H	n-C ₅ H ₁₁	n-C ₅ H ₁₁	H	C ₆ Me ₄ (NC) ₂ -1,4	$< 10^{-12}$				
H	n-C ₆ H ₁₃ O	H	H	C ₆ Me ₄ (NC) ₂ -1,4	$< 10^{-12}$				
H	H	H	H	C ₆ Me ₄ (NC) ₂ -1,4	1×10^{-7}				
H	H	H	H	Pyz	2×10^{-5}	298	0.5 ^c	2.009	
H	H	H	H	Tz	2×10^{-2}	298	0.13	2.23	
H	Me	Me	H	Pyz	9×10^{-6}				
H	Me	Me	H	Tz	1×10^{-3}				
H	H	H	H	Me ₂ Tz	4×10^{-3}				
H	CN	CN	H	Pyz	5×10^{-9}				
H	CN	CN	H	Tz	1×10^{-6}				
H	Bu ^t	H	H	Pyz	5×10^{-11}				
H	Bu ^t	H	H	Tz	9×10^{-9}				
H	Et	H	H	Pyz	8×10^{-9}				
H	Et	H	H	Tz	2×10^{-4}				
H	H	H	H	dabco	1×10^{-9}				
H	H	H	H	bipy	2×10^{-8}	298	0.24	2.00	
Doped phthalocyanines									
H	H	H	H	Pyz	4×10^{-2}				doped with (BF ₄) _{0.45n}
H	H	H	H	Pyz	3×10^{-2}				(PF ₆) _{0.5n}
H	H	H	H	Pyz	1×10^{-5}				(HSO ₄) _{0.4n}
H	H	H	H	Pyz	1×10^{-6}				(SCN) _{0.3n}
H	H	H	H	Pyz	3×10^{-3}				(ClO ₄) _{0.3n}
H	H	H	H	Pyz	2×10^{-1}				I _{2.5n}
H	H	H	H	C ₆ H ₄ (NC) ₂ -1,4	7×10^{-3}				I _{1.4n}
H	H	H	H	C ₆ H ₄ (NC) ₂ -1,4	3×10^{-2}				I _{3.0n}
H	H	H	H	C ₆ Me ₄ (NC) ₂ -1,4	1×10^{-3}				I _{1.5n}
H	H	H	H	C ₆ Me ₄ (NC) ₂ -1,4	2×10^{-2}				I _{3.0n}
H	n-C ₅ H ₁₁	n-C ₅ H ₁₁	H	C ₆ Me ₄ (NC) ₂ -1,4	9×10^{-7}				I _{1.8n}
H	n-C ₆ H ₁₃ O	H	H	C ₆ Me ₄ (NC) ₂ -1,4	2×10^{-10}				I _{2.5n}
1,2-Naphthalocyanine									
H	H	H	H	C ₆ H ₄ (NC) ₂ -1,4	6×10^{-10}				λ_{max} 712, 387; ν_{NC} 2090
2,3-Naphthalocyanines (R ⁵ = R ⁶ = H)									
H	H	H	H	C ₆ H ₄ (NC) ₂ -1,4	2×10^{-3}	293	0.13	0.58	ν_{NC} 2124
n-C ₆ H ₁₃ O	H	H	H	C ₆ H ₄ (NC) ₂ -1,4	4×10^{-6}	82	0.17	0.51	λ_{max} 771, 690 sh, 346; ν_{NC} 2102
H	n-C ₆ H ₁₃ O	H	H	C ₆ H ₄ (NC) ₂ -1,4	1×10^{-5}	82	0.18	0.47	λ_{max} 778, 692 sh, 365; ν_{NC} 2093
H	n-C ₆ H ₁₃ O	n-C ₆ H ₁₃ O	H	C ₆ H ₄ (NC) ₂ -1,4	2×10^{-6}				λ_{max} 765, 686, 359; ν_{NC} 2095
H	H	H	H	Pyz	5×10^{-5}	298	0.26	1.90	
H	H	H	H	Tz	0.3	298	0.19	1.97	

Note. Tz is tetrazine, Me₂Tz is dimethyltetrazine, dabco is 1,4-diazabicyclo[1.2.2]octane, bipy is 2,2'-bipyridyl; ^a relative to metallic iron; ^b ν_{NC} in cm⁻¹, λ_{max} (electronic absorption spectrum) in nm; ^c relative to sodium nitroprusside.

$\text{Fe} \rightarrow \text{TAP} [e_g(d\pi) \rightarrow e_g(\pi^*)]$ charge transfer.⁵⁸ However, this assignment has recently come under strong criticism and this band was attributed^{120, 121} to the $\text{Fe} \rightarrow \text{TAP} [e_g(d\pi) \rightarrow b_{1u}(\pi^*)]$ charge transfer. In the electronic absorption spectra of the $\text{TAP}^{\text{R}}\text{FeL}_2$ complexes containing alkylamines or the cyanide ion as the axial ligands, the intensity of the charge-transfer band at 500 nm is virtually equal to that of the Q band. However, taking into account that the above-mentioned complexes were not characterised by other spectroscopic methods, these data must be considered with caution.^{120–122}

Among complexes of iron naphthalocyanines, compounds containing isocyanide axial ligands have been studied in most detail (Table 9).^{48, 94, 123–126}

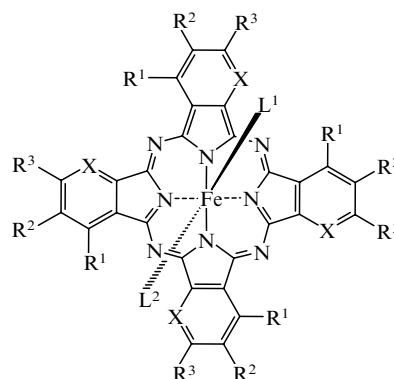


Table 8. Characteristics of the TAP^RFeL₂ complexes (R¹ = R² = Et or Ph).

R	L	Positions of bands in electronic absorption spectra/nm (log ε)	Relative intensity	Ref.
Ph	CN	643(4.39), 572(4.38), 451 sh, 383(4.46) (see ^a) 643(4.27), 574(4.59), 457 sh, 374(4.62) (see ^b)		122
Ph	Py	610, 595 sh, 571, 513, 483 sh, 434 sh, 364	0.97 : 0.3 : 0.33 : 1	58
Ph	4-MeC ₅ H ₄ N	621, 599 sh, 571, 519, 485 sh, 422 sh, 363	0.84 : 0.33 : 0.33 : 1	58, 120, 121
Ph	4-EtC ₅ H ₄ N	621, 599 sh, 571, 517, 483 sh, 424 sh, 361	0.8 : 0.4 : 0.29 : 1	58
Ph	3,4-Me ₂ C ₅ H ₃ N	621, 595 sh, 575 sh, 520, 424 sh, 365	0.77 : 0.34 : 1	58
Ph	4-CH ₂ =CHC ₅ H ₄ N	621, 595 sh, 570, 510, 481, 425 sh, 362	0.75 : 0.33 : 0.33 : 0.35 : 1	58
Ph	3-ClC ₅ H ₄ N	616, 592 sh, 567, 488, 454, 423, 362	0.89 : 0.36 : 0.31 : 0.37 : 0.42 : 1	58
Ph	4-ClC ₅ H ₄ N	615, 592 sh, 568, 424 sh, 356	0.69 : 0.25 : 1	58
Ph	Im	627, 599 sh, 575 sh, 539, 445 sh, 366	0.69 : 0.48 : 1	58, 120, 121
Ph	MeIm	629, 581 sh, 539, 450 sh, 365	0.77 : 0.43 : 1	58
Ph	PhNH ₂	627, 602 sh, 581 sh, 530, 450 sh, 370	0.53 : 0.34 : 1	58
Ph	NH ₃	631, 602 sh, 585 sh, 537, 424 sh, 365	0.68 : 0.37 : 1	58
Ph	Pip	629, 602 sh, 581 sh, 537, 420 sh, 366 623, 535, 367	0.68 : 0.45 : 1 0.52 : 0.44 : 1 (see ^c)	58
Ph	cyclo-C ₆ H ₁₁ NH ₂	631, 606 sh, 585 sh, 536, 420 sh, 363	0.53 : 0.35 : 1	58
Ph	Pr ⁿ NH ₂	627, 545, 371	0.82 : 0.70 : 1 (see ^c)	120, 121
Ph	Pr ⁿ NH	622, 538, 364	0.82 : 0.49 : 1 (see ^c)	120, 121
Ph	Et ₂ NH	622, 536, 364	0.81 : 0.56 : 1 (see ^c)	120, 121
Ph	Mor	623, 533, 365	0.81 : 0.59 : 1 (see ^c)	120, 121
Ph	n-C ₅ H ₁₁ NH ₂	628, 541, 366	0.83 : 0.71 : 1	120, 121
Et	Py	586, 564 sh, 541, 458, 332 (see ^d)		57
Et	MeIm	590, 574 sh, 550 sh, 491, 333, 315 sh (see ^e)		57

^a In CH₂Cl₂; ^b in acetone; ^c in acetonitrile; ^d in PhH–Py; ^e in PhH.

Four structural isomers are possible for derivatives of 1,2-Nc^RFeL₂. An individual isomer, which contains the *tert*-butylisocyanide and cyclohexylisocyanide ligands and is characterised by C_{4h} symmetry, was isolated and its structure was established.^{48,49} Due to the strong π-acceptor properties of the axial ligands, the Fe–C_{ax} bond length is smaller than the Fe–N(Pc) distance (see Table 1). On the whole, the spectral characteristics and properties of the 1,2-Nc^RFeL₂ complexes are very similar to those of Pc^RFeL₂ (see Tables 4–7). In the 2,3-Nc^RFeL₂ complexes, linear

annellation of an additional benzene ring (contrary to angular annellation resulting in 1,2-NcFe) leads to a sharp change in the properties of these compounds, which is manifested, for example, in a strong bathochromic shift of the Q band in the electronic absorption spectra and in enhancement of the semiconducting properties (see Tables 7 and 9, Fig. 2).^{9,13,110,112} An extension of the π-system of the macrocycle leads to a decrease in the stability of the complexes containing the 2,3-Nc^RFe fragment.^{123–126}

Table 9. Properties of axially coordinated complexes of iron naphthalocyanines and pyridinoporphyrines.

R ¹	R ²	R ³	X	L	Positions of bands in electronic absorption spectra /nm	ν _{NC} /cm ⁻¹	Ref.
1,2-Naphthalocyanines							
CH = CHCH = CH	H	CH	Bu ⁿ NC		653, 594, 353	2140	48
			cyclo-C ₆ H ₁₁ NC		654, 594, 354	2155	
			Bu ⁿ NC		654, 595, 354	2153	
CH = CBu ⁿ CH = CH	H	CH	Py		666, 604, 353		49
			Bu ⁿ NC		662, 602, 354		
CH = CMeCH = CH	H	CH	Py		668, 606, 354		49
CH = CPhCH = CH	H	CH	Py		670, 607, 364		49
2,3-Naphthalocyanine							
H	CH = CHCH = CH	CH		C ₆ H ₄ (NC) ₂ -1,4		2145	94
Tetrakis(2,3-pyridino)porphyrines							
H	H	H	N	Bu ⁿ NC	627, 573, 339	2157	91
				cyclo-C ₆ H ₁₁ NC	628, 574 sh, 398 sh, 339	2171	
				PhNC	633, 577 sh, 332	2141	
				Me ₂ C ₆ H ₃ NC	632, 577 sh, 393 sh, 331	2140	
				<i>o</i> -MeC ₆ H ₄ NC	634, 579 sh, 393 sh, 331	2136	
				<i>m</i> -MeC ₆ H ₄ NC	634, 580 sh, 330	2134	
				<i>p</i> -MeC ₆ H ₄ NC	633, 579 sh, 391 sh, 332	2144	
				<i>p</i> -Pr ⁱ C ₆ H ₄ NC	634, 579 sh, 394 sh, 332	2144	

Complexes of iron tetrakis(2,3-phenanthro)porphyrizine were prepared by photochemical oxidation of *trans*-1,2-dicyano-1,2-diphenylethylene in the presence of iodine followed by template condensation with iron compounds and axial coordination with different isocyanides.¹²⁷ These complexes were characterised by electronic and Mössbauer spectroscopy. In addition, complexes of iron tetrakis(2,3-pyridino)porphyrizine with isocyanides as axial ligands were prepared and characterised (see Table 9).⁹¹

2. Iron(III) complexes

In spite of the fact that azaporphin iron(III) complexes have been considered in the literature over several decades, convincing evidence for the existence of Pc complexes of iron(III) has been reported, and furthermore their properties, have been described only recently. Oxidation of a solution of $\text{Na}_2[\text{PcFe}^{\text{II}}(\text{CN})_2]$ in dichloromethane with bromine afforded the six-coordinate $\text{Na}[\text{PcFe}^{\text{III}}(\text{CN})_2]$ complex.⁵⁵ In the electronic absorption spectra, this process is characterised by distinct isosbestic points (Fig. 3). The $\text{Na}[\text{PcFe}^{\text{III}}(\text{CN})_2]$ complex can also be prepared by oxidation of $\text{Na}_2[\text{PcFe}^{\text{II}}(\text{CN})_2]$ with cumene hydroperoxide¹²⁸ or by the reactions of $\text{Na}[\text{PcFe}^{\text{III}}(\text{OH})_2]$ with cyanides.⁵⁰ The $[\text{PcFe}^{\text{III}}(\text{CN})_2]^-$ complex was characterised in detail by electronic absorption, Mössbauer, IR, Raman, ESR and circular dichroism spectra, magnetic susceptibility data and X-ray diffraction analysis (Table 10).^{50, 55, 129} The magnetic susceptibilities, the parameters of the Mössbauer spectra and the character of the electronic absorption spectra demonstrate that this compound can be described as a low-spin ($S = 1/2$) iron(III) complex with the $(d_{xy})^2(d_{xz}, d_{yz})^3$ electronic configuration. The presence of a hole in the d_π orbital of the central atom results in the appearance of a series of $\text{L}(\text{Pc})-\text{Fe}$ charge-transfer bands in the electronic absorption spectra. The most detailed assignment of the bands in the electronic absorption spectrum of the $\text{Na}[\text{PcFe}^{\text{III}}(\text{CN})_2]$ complex was made by Ough and Stillman.⁵⁵ Based on the analysis of the magnetic circular dichroism and electronic absorption spectra, two $\text{Fe} \rightarrow \text{L}(\text{Pc})$ and four $\text{Fe} \rightarrow \text{Pc}$ charge-transfer bands were identified.⁵⁵ According to the data from X-ray diffraction analysis⁵⁰ (see Table 1), the $\text{Fe}-\text{C}_{\text{ax}}$ bond length in $\text{PNP}[\text{PcFe}^{\text{III}}(\text{CN})_2]$ is larger than the $\text{Fe}-\text{N}(\text{Pc})$ bond length. This complex is more similar in structure to compounds of the $\text{PcFe}^{\text{II}}\text{L}_2$ type with nitrogen-containing axial ligands^{43–46} and differs from analogous complexes with axial ligands exhibiting strong π -acceptor properties.^{48, 49} The reactions of $[\text{PcFe}^{\text{III}}(\text{CN})_2]^-$ with pyridine and imidazole afforded compounds with composition $\text{PcFe}^{\text{III}}(\text{CN})\text{L}$, whereas the reaction with hydrazine was accompanied by reduction of the iron ion to form

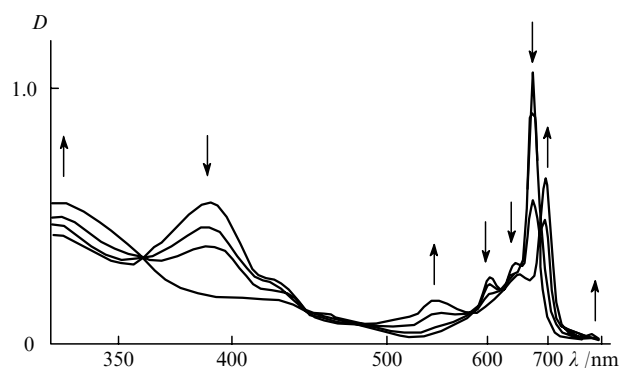


Figure 3. Dynamics of oxidation of the $[\text{PcFe}^{\text{II}}(\text{CN})_2]^{2-}$ complex with cumene hydroperoxide to form $[\text{PcFe}^{\text{III}}(\text{CN})_2]^-$.

$[\text{PcFe}^{\text{II}}(\text{CN})(\text{N}_2\text{H}_4)]^-$.⁵⁰ Complexes of the $\text{PcFe}^{\text{III}}(\text{CN})\text{L}$ type can also be prepared by the reactions of the ligand L with the cyanide complex $[\text{PcFe}^{\text{III}}(\text{CN})]^-$.¹³⁰ The reactions of $\text{Na}[\text{PcFe}^{\text{III}}(\text{CN})_2]$ with acids yielded complexes of the $\text{Pc}^+ \text{Fe}^{\text{III}}(\text{CN})\text{X}$ type containing the phthalocyanine radical cation. Finally, $\text{Na}[\text{PcFe}^{\text{III}}(\text{CN})_2]$ can be reduced to the cyanide iron(II) complex under the action of different reducing agents.⁵⁰

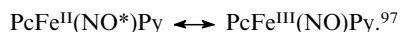
Complexes of the general formula $\text{PNP}(\text{PcFe}^{\text{III}}\text{XY})$ ($\text{X} = \text{Y}$) were synthesised^{89, 129} and characterised by electronic absorption, Mössbauer and ESR spectra as well as by magnetic susceptibility data (see Table 10). These compounds exhibit the following characteristic features: (1) the electronic absorption spectra of all complexes have additional $\text{Pc} \rightarrow \text{Fe}$ and $\text{Fe} \rightarrow \text{Pc}$ charge-transfer bands in the region of 400–800 nm, and the Q band is bathochromically shifted compared to that for the PcFeL_2 complexes; (2) in most cases, the electronic absorption spectra are typical of axially coordinated low-spin ($S = 1/2$) iron(III) complexes;^{131, 132} (3) in all the studied complexes, except for the cyanide complex, the quadrupole doublets in the Mössbauer spectra are characterised by substantial asymmetry; a low-intensity broad component of the doublet for the complexes with the $\text{Fe}-\text{O}_{\text{ax}}$ bond is observed at low rates, whereas this component for the complexes with the $\text{Fe}-\text{N}_{\text{ax}}$ bonds is observed at higher rates,¹²⁹ as in the case of the well-studied iron(III) complexes with porphyrin ligands^{100, 133} {for the azide complex anion $[\text{PcFe}^{\text{III}}(\text{N}_3)]^-$, the sign of the electric field gradient was found to be negative¹³⁴}; (4) magnetic moments for all the complexes studied are in the range of 2.0–2.5 μ_{B} at room temperature. Based on the data from mag-

Table 10. Physicochemical properties of the $[\text{PcFe}^{\text{III}}\text{XY}]^n$ complexes ($S = 1/2$).^{89, 128, 130}

<i>n</i>	X	Y	<i>T</i> /K	δ^a /mm s ⁻¹	ΔE_Q /mm s ⁻¹	μ/μ_{B} (<i>T</i> /K)	Factor <i>g</i> in ESR spectra	Positions of bands in electronic absorption spectra /nm
–1	OH	OH	4.2	0.18	2.22	2.31 (300) 2.06 (4.2)	2.31, 2.11, 1.96	800, 690, 630, 575, 450, 360
–1	OPh	OPh	4.2	0.22	2.64	2.3 (300)	2.31, 2.12, 1.93	
–1	NCO	NCO	4.2	0.29	2.25	2.44 (300) 1.96 (4.2)	broad lines	775, 685, 673, 655, 645, 610, 555, 435, 375, 330, 280
–1	NCS	NCS	4.2	0.26	2.65	2.4 (300)	the same	790, 690, 673, 645, 610, 565, 525, 485, 385, 330
–1	N ₃	N ₃	4.2	0.21	2.49	2.05 (300) 1.76 (4.2)	2.41, 2.07, 1.79	
–1	CN	CN	4.2	0.11	0.99	2.49 (300) 1.89 (4.2)	2.41, 2.07, 1.79 2.00 (broad peak)	775, 685, 650, 620, 600, 540, 500, 425, 400, 322 781, 755, 688, 663, 646, 623, 603, 545, 421, 399, 325, 285
0	Py	CN	293	0.04	1.57			783, 690, 651, 595, 555, 510, 412, 317 (see ^b)
0	Bu ^t Py	CN	293	0.04	1.57			see ^c
0	Pyz	CN	293	0.05	1.60			

^a Relative to sodium nitroprusside; ^b $\nu_{\text{CN}} 2131 \text{ cm}^{-1}$, $\sigma_{\text{RT}} = 1 \times 10^{-10} \text{ S cm}^{-1}$; ^c $\nu_{\text{CN}} 2132 \text{ cm}^{-1}$, $\sigma_{\text{RT}} = 6 \times 10^{-5} \text{ S cm}^{-1}$.

netic circular dichroism and electronic absorption spectroscopy, it was concluded⁵⁵ that the phthalocyanine ligand in the $[\text{PcFe}^{\text{II}}(\text{CN})_2]^{2-}$ complex behaves as a σ -donor and a π -acceptor and the result of oxidation of the iron ion yielding $[\text{PcFe}^{\text{III}}(\text{CN})_2]^-$ is that the phthalocyanine ligand behaves as a σ - and π -donor. Of special note is the $\text{PcFe}^{\text{III}}(\text{NO})\text{Py}$ complex, which was prepared by a ligand exchange reaction. Based on the data from magnetic susceptibility and Mössbauer spectroscopy, this complex should be assigned to low-spin ($S = 1/2$) iron(III) compounds. For this complex, two isomeric forms that differ in the site of localisation of the electron hole are possible:



Polymeric iron(III) complexes linked through bridging ligands, viz., $[\text{PcFe}^{\text{III}}(\text{CN})]_n$, $[2,3\text{-NcFe}^{\text{III}}(\text{CN})]_n$ and $[\text{PcFe}^{\text{III}}(\text{SCN})]_n$, were synthesised^{110,112} analogously to polymeric iron(II) complexes. The resulting polymers are characterised by high thermal stabilities (up to 250 °C) and rather high conductivities at room temperature (10^{-5} – 10^{-3} S cm⁻¹).

The octaphenyl complex $(\text{Bu}_4\text{N})[\text{TAP}^{\text{Ph}}\text{Fe}^{\text{III}}(\text{CN})_2]^{122}$ is the only tetraazaporphin complex of this type characterised by IR and electronic absorption spectroscopy and elemental analysis. Oxidation of the Fe^{2+} ion in this complex to the Fe^{3+} ion, unlike oxidation of the corresponding phthalocyanine complexes, results in a hypsochromic rather than bathochromic shift of the Q band.

3. 'Acidic' complexes of iron phthalocyanine and its analogues

Barrett and coworkers¹⁷ were the first to prepare the so-called 'chlorine-containing' PcFe complex by heating PcFe with concentrated hydrochloric acid. This compound was also synthesised by the reaction of the PcFe μ -oxo dimer,^{6,56,135} $\text{PcFe}(\text{en})_2$ complexes,⁵⁰ where en is ethylenediamine, or the $\text{PNP}[\text{PcFe}^{\text{III}}(\text{OH})_2]$ complex^{89,129} with hydrochloric acid as well as in a direct reaction, for example, upon boiling of a mixture of anhydrous FeCl_3 with phthalonitrile in 1-chloronaphthalene.⁸⁹

Originally, a structure with the chlorine atom at the Fe^{III} atom, viz., $\text{PcFe}^{\text{III}}\text{Cl}$ (**1**), was assigned to the resulting compound.¹⁷ However, Lever⁵³ gave preference to the hydrochloride structure $\text{PcFe}^{\text{II}}\cdot\text{HCl}$ (**2**), because an attempt to sublime the resulting complex *in vacuo* resulted in the formation of PcFe and elimination of hydrogen chloride. Later, Lever, on the basis of magnetic susceptibility data, returned to the initial hypothesis that the complex has the structure of 'chlorine-containing' iron(III) phthalocyanine.⁵² Since then, the above-considered notions of the structures of these compound and analogous five-coordinate complexes with axial acido ligands X co-exist. Thus on the basis of spectral data alone (Table 11), 'acidic' complexes of iron phthalocyanine were assigned to iron(III) derivatives with the mixed-spin ($S = 5/2 - 3/2$) electronic state (structure **1**).^{89,129} Based on the chemical properties and spectral data, these complexes were alternatively considered as iron(II) derivatives with intermediate ($S = 1$) spin (structure **2**),^{6,7,56,136-138} and it was

believed that the proton is most likely localised on the pyrrolenine nitrogen atom.^{6,138}

The electronic absorption spectra of the HPcFeX complexes are characterised by the presence of a charge-transfer band (at ~ 820 – 860 nm) in the near IR region along with an intense Q band in the long-wavelength region (at ~ 660 nm). The position of this charge-transfer band depends on the nature of the ligand X (see Fig. 1, Table 11).^{56,89} The presence of the low-energy charge-transfer band in the near IR region is easily explained in the framework of both structures described above. The position of the Q band in the spectra of HPcFeX virtually coincides with those in the electronic absorption spectra of the $\text{PcFe}^{\text{II}}\text{L}_2$ (see Refs 47 and 68–77) and $\text{PcFe}^{\text{II}}\text{L}(\text{DMSO})$ ⁷⁹⁻⁸⁴ complexes and differs substantially from the position of the Q band in the electronic absorption spectra of the bisaxially coordinated iron(III) complexes $[\text{PcFe}^{\text{III}}\text{X}_2]^-$ (see Table 10).^{89,129} In the Mössbauer spectra (see Table 11) of the 'acidic' complexes, the ΔE_{Q} values are very large, which is untypical of both high- and low-spin iron(III) complexes with macrocyclic ligands.^{86,99,100,103,139} However, these values correlate well with the hypothesis that the iron ions in these complexes exist in an intermediate spin state ($S = 3/2$).^{99,100,103} The only principal fact, which is inconsistent with this suggestion, is that the asymmetry of the doublet, which is characteristic of iron(III) complexes, is absent in the Mössbauer spectra.^{100,133} At the same time, the parameters of the Mössbauer spectra of the 'acidic' complexes are similar to those of the iron(II) complexes containing macrocyclic ligands and the iron ion in the intermediate spin state ($S = 1$).^{99,100,103} The electronic absorption spectra and magnetic susceptibility data of the 'acidic' complexes are available only for unsubstituted phthalocyanines (see Table 11).^{89,129} Unlike the low-spin $[\text{PcFe}^{\text{III}}\text{X}_2]^-$ complexes whose electronic absorption spectra are typical of the d^5 electronic configuration (see Table 10),¹²⁹ most of the 'acidic' complexes either give broad lines or do not give signals at all. The spectra of solid samples differ from each other (see Table 11). Moreover, even the complexes with the same ligand X gave different spectra.¹²⁹ At the same time, the electronic absorption spectra of the analogous high-spin porphyrin complexes¹⁰⁰ and the corresponding porphyrazine complexes containing iron in the intermediate spin state (which are considered below) both in frozen matrices and in the solid state are identical and typical of axial iron(III) complexes. However, if the structure **2** is correct, the electronic absorption spectra should not be observed due to the rapid spin-lattice relaxation typical of paramagnetic iron(II) complexes.¹³² Based on the data from magnetic susceptibility (see Table 11), the 'acidic complexes' were assigned to compounds in which the central iron ions are in the mixed-spin ($S = 3/2 - 5/2$) electronic state^{89,129} because the magnetic susceptibilities differ from the spin-only values ($S = 3/2 \mu_{\text{B}} = 3.87$; $S = 5/2 \mu_{\text{B}} = 5.92$). However, the experimental values are close to those for iron(II) complexes with intermediate spin in the case of strong coupling between ground state spin and orbital angular momenta.⁵¹⁻⁵³ For example, the magnetic susceptibilities of the

Table 11. Spectral characteristics of 'acidic' complexes of iron phthalocyanine of the HPcFeX type.^{56,129}

X	Positions of bands in electronic absorption spectra /nm	δ (4.2 K) /mm s ⁻¹	ΔE_{Q} (4.2 K) /mm s ⁻¹	$\mu_{\text{eff}} / \mu_{\text{B}}$		Factor g in ESR spectra
				300 K	4.2 K	
F	832, 758, 710, 655, 615, 600, 465, 368					
Cl	832, 758, 655, 595, 485, 450	0.28	2.94	4.53	3.25	4.67, 2.0
Br	840, 710, 658, 590, 450	0.28	3.12	4.09	3.2	broad lines
I	848, 710, 690, 595, 465	0.28	3.23	3.62	2.32	—
CF ₃ CO ₂		0.28	3.08	4.08	3.39	signal was not observed
CCl ₃ CO ₂		0.29	3.07	3.90	3.06	2.0
HCO ₂				4.09		~ 6.3 , ~ 4.3
CF ₃ SO ₃				4.14		signal was not observed
Ts				4.17		the same

Table 12. Spectral characteristics of the TAP^RFeX complexes ($R^1 = R^2 = \text{Et, EtS or Ph}$).^{140, 142–144}

R	X	Positions of bands in electronic absorption spectra /nm	T^a /K	δ /mm s ⁻¹	ΔE_Q /mm s ⁻¹	Factor g in ESR spectra	μ_{eff}/μ_B	Data of X-ray diffraction analysis (bond lengths /Å)		
								Fe–X	Fe–N ₄	Fe–N
Et	Cl	318, 364, 436, 555, 672	298	0.28	2.98	3.98, 1.99	3.89	2.278	0.352	1.929
			80	0.37	3.0					
Et	ClO ₄	312, 375, 497, 582, 711	300	0.35	4.38	3.98, 1.99	3.87	2.091	0.263	1.913
Et	PF ₆	312, 372, 505, 558, 687	300	0.3	4.02	4.05, 2.04	3.44–3.94			
Et	SbF ₆	322, 372, 509, 588, 722				4.07, 2.01	3.55–3.79			
Et	CF ₃ CO ₂	310, 371, 445, 566, 684	300	0.23	3.36	3.55, 2.01	3.80–4.06			
Ph	F	665, 533, 435, 318	300	0.2	3.0					
			140	0.28	2.99					
			82	0.29	2.97					
Ph	Cl	709, 544, 431, 335	300	0.23	2.15		3.44			
			82	0.26	2.85					
Ph	Br	716, 548, 432, 329	300	0.19	2.75		2.98; 4.66 ^b			
			82	0.25	3.04					
Ph	I	723, 561, 444, 328	300	0.19	3.21					
			82	0.24	3.39					
Ph	HSO ₄	721, 563, 440, 329	300	0.16	3.25					
			82	0.28	3.58					
EtS	Cl					4.3, 2.36; ^b 2.17, 1.96; ^b 3.92, 1.96 ^b		2.308	0.286	1.936
Et	NO	590, 350, 316	100	0.21	1.95	1.99		1.931	0.308	1.721

^a Temperature at which the Mössbauer spectra were recorded; ^b data from different studies.

PcFe complexes, iron octaethylporphyrine and iron tetraphenylporphyrin at room temperature (3.85,^{51–53} 3.82⁵⁷ and 4.4 μ_B ,¹³⁹ respectively) are close to the μ_{eff} values for the ‘acidic’ complexes (see Table 11). The chemical behaviour of the ‘acidic’ complexes, *viz.*, the elimination of HCl and the formation of PcFe upon sublimation of the ‘chlorine-containing’ PcFe complex,⁵³ the absence of products of radical nature and hydrogen in the reaction of PcFe with HCl,^{6, 56} the formation of ‘acidic’ complexes from the μ -oxo iron(II) dimer (the form 690)^{56, 135} and the absence of redox-conversion products, indicate that the iron ions in these complexes exist, most likely, in the divalent rather than trivalent state. Moreover, the reactions of the μ -oxo PcFe(III) dimer (the form 630) with acids afforded unstable products whose electronic absorption spectra are quite different from those of the ‘acidic’ complexes.⁷

Therefore, taking into account all the above-considered facts, the structure **2** seems to be preferable. However, the unambiguous elucidation of the structures of ‘acidic’ complexes of readily soluble PcFe derivatives calls for further investigations of these compounds both by physical (primarily, electronic absorption spectroscopy and magnetic susceptibility studies) and chemical methods.

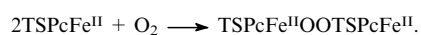
In the series of ‘acidic’ porphyrine iron complexes, octaethyl-,^{57, 140} octaphenyl-^{141, 142} and octa(ethylthio)porphyrine¹⁴³ derivatives were studied. These complexes were prepared either by the reactions of the corresponding μ -oxo dimers^{57, 141–143} or anionic dihydro complexes¹⁴³ with acids or by ligand exchange reactions.¹⁴⁰ Based on the data from magnetic susceptibilities and on the parameters of the Mössbauer and electronic absorption spectra in frozen matrices (Table 12), the octaethyl- and octaphenylporphyrine complexes were assigned to iron(III) derivatives with intermediate ($S = 3/2$) spin. This assignment is consistent with the data from X-ray diffraction analysis (see Table 12).^{57, 140} However, the chemical properties and the electronic absorption spectra of ‘acidic’ complexes of *tert*-butyl-substituted analogues⁶ can be better explained on the basis of the structure **2**. Therefore, we believe that final conclusions cannot be made.

An unusual coordination about the central atom was observed in the ‘acidic’ complex of octa(ethylthio)porphyrine.¹⁴³ According to the data from X-ray diffraction analysis, the coordination sphere about the central atom is formed by four nitrogen atoms of the macrocyclic ligand, the chloride ion and the sulfur atom of the peripheral substituent of the adjacent molecule. The different behaviour of this complex in the polycrystalline state and in solution was attributed to the differences in the electronic structure of these two states.¹⁴³ Thus it was suggested that the solid complex exists in the mixed-spin ($S = 5/2 - 1/2$) state, whereas this complex in solution was described as in an intermediate-spin state ($S = 3/2$).¹⁴³

Recently, the spectroscopic parameters of the TAP^{Et}Fe(NO) complex, which has been synthesised by reductive nitrosation of the ‘acidic’ TAP^{Et}Fe complex in the presence of 2,6-dimethylpyridine, were reported (see Table 12).¹⁴⁴ These data made it possible to assign the complex under consideration to five-coordinate iron(II) derivatives with an angular structure of the nitrosyl ligand.

IV. μ -Oxo(-nitrido, -carbido) binuclear complexes of iron phthalocyanine and its analogues

In 1965, the reversible addition of oxygen to iron(II) tetrasulfophthalocyanine (TSPcFe^{II}) in aqueous solution yielding a μ -peroxo dimeric complex was reported.¹⁴⁵



However, the structure TSPcFe^{III}X was assigned to the product of the reaction of TSPcFe^{II} ($\lambda_{\text{max}} = 670$ nm) with oxygen ($\lambda_{\text{max}} = 630$ nm), although attempts to isolate and characterise this product have failed.^{146, 147} In 1971, specimens of PcFe synthesised by different procedures were studied by Mössbauer spectroscopy and it was found that the spectra of the products obtained upon treatment of PcFe with 2-picoline in air and upon heating of PcFe in air ($\delta = 0.29$ and 0.348 mm s⁻¹, $\Delta E_Q = 0.36$ and 1.13 mm s⁻¹, respectively) differ substantially from the spectra of the initially freshly prepared PcFe ($\delta = 0.385$ mm s⁻¹, $\Delta E_Q = 2.58$ mm s⁻¹).⁹⁸ In the following, we will demonstrate

that the first two complexes described as 'other forms of PcFe'⁹⁸ are actually μ -oxo dimeric iron complexes.

More recently, in attempting to isolate Pc^IFe by chromatography, Bundina *et al.*⁵⁶ obtained an oxygen-containing compound as the major product. Its molecular weight was approximately twice as large as that of Pc^IFe and its spectral characteristics differed significantly from those reported for PcFe and its substituted analogues. Based on the spectral data and the chemical properties of chromatographically pure specimens, it was suggested that the compound under consideration had the structure of the μ -oxo dimer with an Fe—O—Fe bridge analogous to the structures of the well-studied μ -oxo dimeric porphyrin iron complexes.^{148–151} In the first study,⁵⁶ the authors considered two alternative structures for the μ -oxo dimeric PcFe complexes, *viz.*, PcFe^{III}OFe^{III}Pc (**3**) and HPcFe^{II}OFe^{II}PcH (**4**), which differ in the oxidation state of the iron atom. Based on the data from elemental analysis and IR, X-ray photoelectron and electronic absorption spectroscopy as well as on the chemical behaviour of this complex, preference was given to the structure **4**. It was suggested that the hydrogen atoms were located at the pyrrolenine nitrogen atoms of the phthalocyanine ligands.^{56, 152}

In 1979, a stable dimeric complex was prepared by the reaction of PcFe with oxygen in DMSO or DMF, and the structure of the μ -peroxo dimer PcFe^{III}OOFc^{III}Pc was assigned to the resulting compound.¹⁵³ However, thereafter this suggestion was rejected^{154, 155} based on spectroscopic data, in particular, on the IR spectra of the complex containing the ¹⁸O isotope in the μ -bridge, and the μ -oxo dimeric structure was proposed. Taking into account the results of volumetric analysis of oxygen absorption by the PcFe complex, the structure **3** with the central iron(III) ions was assigned to the μ -oxo dimer. This point of view has received support from many researchers.^{135, 156–162} At present, this view predominates in spite of the fact that it has recently come under strong criticism.^{7, 128, 163} Although μ -oxo dimeric complexes belong to one of the most stable coordination forms of PcFe, their electronic structures are still questionable. In this connection, let us consider the properties of these complexes in more detail.

The μ -oxo dimeric PcFe complex can be prepared according to the following procedures: (1) by bubbling air or oxygen through a solution of PcFe in sulfuric acid, as well as in DMSO, DMF or

other organic solvents;^{56, 154, 155} (2) by short-term boiling of a suspension of PcFe with sterically hindered aliphatic amines¹⁵⁷ or α -pyridines⁹⁸ in the medium of the amine or in organic solvents; (3) the solid-phase reaction of PcFe with oxygen with heating;⁹⁸ or (4) dimerisation of monomeric bisaxially coordinated PcFe complexes.^{89, 156} The IR spectra of the μ -oxo dimeric PcFe complex have bands at 851 and 822 cm^{−1}, which were assigned to vibrations of the Fe—O—Fe fragment.^{56, 135, 155–157} μ -Oxo dimeric Pc^RFe complexes were prepared by chromatography of the Pc^RFe complexes (using eluents which did not contain potential ligands, such as organic bases or acids)^{56, 135, 152, 163} or according to one of the above-mentioned procedures for the synthesis of the μ -oxo dimer of PcFe.

In the electronic absorption spectra of μ -oxo dimeric PcFe complexes in noncoordinating solvents, the Q and B bands are bathochromically shifted compared to their positions in the spectra of other forms of PcFe (Table 13). This behaviour is untypical of μ -oxo dimeric phthalocyanine complexes of other metals.⁶² The Q band is observed at 700 nm. In all cases, this band is broadened and has a short-wave shoulder.^{6, 7, 56, 135, 152} To explain the bathochromic shift on the basis of the theory of exciton splitting, it was assumed that the phthalocyanine ligands in these complexes are nonparallel or are shifted relative to each other (slipped-stack),¹²⁸ which is untypical of the μ -oxo dimeric iron(III) complexes.^{148, 149}

The unusual geometry of the μ -oxo dimeric PcFe complexes was confirmed by ¹H and ¹³C NMR spectroscopy. As was noted in a number of studies,^{6, 7, 56, 128} the spectra of these compounds are more complicated than those of other PcFe forms containing the μ -oxo fragment (see below) and are similar to those of μ -oxo dimeric silicon phthalocyanines.¹⁶⁴ The spectral patterns indicate that the protons of the peripheral substituents are substantially nonequivalent. This nonequivalence can be explained only on the assumption that the geometry of the μ -oxo dimeric PcFe complexes differs substantially from that typical of other μ -oxo dimeric iron complexes with macrocyclic ligands (the Fe—O—Fe angle is close to 180° and the macrocycles are parallel to each other^{148, 149}).

μ -Oxo dimeric PcFe complexes in the solid state, unlike those in solution, exist as two isomeric forms possessing different

Table 13. Mössbauer and electronic absorption spectra of μ -oxo dimeric PcFe complexes (form 690).

R ¹	R ²	R ³	R ⁴	T ^a /K	δ /mm s ^{−1}	ΔE_Q /mm s ^{−1}	Positions of bands in electronic absorption spectra ^b /nm	Ref.
H	H	H	H	77	0.36 0.25	0.44 1.26		156, 157
H	Bu ^t	H	H	82	0.22 0.33	1.39 0.39	363, 590, 687, 704	56, 128, 135
H	Et	H	H	82	0.22 0.35	1.35 0.45	363, 588, 687, 703	135
H	EtOCH ₂	H	H	100	0.22 0.35	1.34 0.43	290, 358, 600, 692, 704	135
H	CO ₂ Et	H	H	82	0.22 0.33	1.35 0.41	345, 586, 690, 710	135
H	CO ₂ C ₆ H ₁₃ -n	H	H	82	0.22 0.33	1.35 0.53	285, 350, 586, 697, 710	135
H	OCH ₂ CH(Et)Bu ⁿ	H	H	82	0.22 0.36	1.33 0.45	300, 370, 410, 610, 715	135
H	OCH ₂ Bu ^t	H	H	82	0.35	0.41	295, 368, 400, 610, 711	135
H	OCH ₂ C(Me) ₂ Bn	H	H	82	0.22 0.36	1.34 0.41	289, 367, 593, 697, 709	135
H	OC ₈ H ₁₇ -n	OC ₈ H ₁₇ -n	H	82	0.22 0.34	1.34 0.52	300, 360, 425, 600, 670, 714	135
H	OCH ₂ CH(Et)Bu ⁿ	OCH ₂ CH(Et)Bu ⁿ	H	82	0.36	0.52	300, 360, 425, 600, 670, 714	135

^a Temperature at which the Mössbauer spectra were recorded; ^b toluene as the solvent.

properties.^{135, 156, 157} Dimerisation of the monomer $\text{PNP}[\text{PcFe}^{\text{III}}(\text{OH})_2]$ afforded predominantly the so-called oxo(1) isomer of the μ -oxo dimeric PcFe complex, while bubbling of air through an oxo(1) solution in sulfuric acid or short-term heating of PcFe with sterically hindered aliphatic amines or α -substituted pyridines yielded predominantly the oxo(2) isomer.^{89, 129, 156, 157} According to the data from Mössbauer spectroscopy (see Table 13), chromatographically pure specimens of readily soluble μ -oxo dimeric $\text{Pc}^{\text{R}}\text{Fe}$ complexes occur as mixtures of the oxo(1) and oxo(2) isomers, which have not been isolated in the individual state.^{56, 128, 135, 152} The parameters of the Mössbauer spectra of the μ -oxo dimeric $\text{Pc}^{\text{R}}\text{Fe}$ complexes depend only slightly on the nature of the peripheral substituents; however, the electric field gradients have negative and positive signs for the oxo(1) and oxo(2) isomers, respectively. This fact provides additional evidence for the assumption as to the difference in the geometry of the isomers.¹⁶⁵ In addition, the Mössbauer spectra of the μ -oxo dimeric $\text{Pc}^{\text{t}}\text{Fe}$ complex in frozen matrices (for example, in toluene) at 77 K have only one signal belonging to the oxo(1) isomer.⁶ The proponents of the hypothesis for the trivalent state of the central iron atoms believe that the oxo(1) isomer has an angular geometry, whereas the Fe—O—Fe fragment in the oxo(2) isomer is quasi-linear and both isomers are high-spin iron(III) complexes [in the oxo(1) and oxo(2) isomers, $S = 5/2$ for both Fe atoms].¹⁵⁷ The supporters of the concept of the divalent state suggest that the phthalocyanine ligands in the oxo(1) isomer are, most probably, in the slipped-stack orientation, whereas an angular geometry of the ligands is typical of the oxo(2) isomer. Both iron(II) ions of the latter possess intermediate spin ($S = 1$).^{128, 163} In our opinion, the results obtained in magnetic susceptibility studies and the ESR spectra of the μ -oxo dimeric PcFe oxo(1) and oxo(2) complexes are less reliable.^{135, 155–157} The magnetic susceptibilities of different specimens of the oxo(1) and oxo(2) isomers at room temperature vary from 2.19 to 2.23 μ_{B} and from 1.38 to 1.42 μ_{B} , respectively. The antiferromagnetic interaction constants J calculated from the magnetic susceptibilities are -120 and -195 cm^{-1} , respectively.^{156, 157} On the contrary, the results of measurements of the magnetic susceptibilities for ten chromatographically pure readily soluble specimens of the μ -oxo dimeric $\text{Pc}^{\text{t}}\text{Fe}$ complex, which have been synthesised independently,^{6, 56, 152} suggest the diamagnetism of this compound. The magnetic moments are no higher than 0.48 μ_{B} . Therefore, it should be admitted that specimens of the μ -oxo dimeric PcFe complexes studied in Refs 135 and 155–157 are very likely to contain substantial amounts of monomeric high-spin impurities, which introduce errors into the true values of magnetic susceptibility. This conclusion agrees well with the data from ESR and Mössbauer spectroscopy.^{156, 157, 163} The ESR spectra of powders of μ -oxo dimeric PcFe complexes at the boiling temperatures of nitrogen or helium have signals with a g factor of ~ 6 , which is characteristic of monomeric high-spin iron(III) complexes. Some specimens give additional signals with a g factor of ~ 4.3 , characteristic of monomeric complexes of iron(III) in the intermediate ($S = 3/2$) spin state.^{7, 132} The ESR spectrum of a powder of the μ -oxo dimeric $\text{Pc}^{\text{t}}\text{Fe}$ complex at 77 K has a set of lines with a g factor approximately equal to 2.¹³⁵ Under analogous conditions, very weak signals with a g factor approximating 6 were additionally observed for this compound.¹⁶³ It should be noted that all ESR data were obtained only for powdered samples. However, as has been mentioned many times,^{128, 166} the ESR spectra of the phthalocyanine complexes in the solid state should be considered with caution. Thus signals with g factors close to 2 were observed for many diamagnetic phthalocyanines in the solid phase.¹⁶⁶ Moreover, the lack of reliable data of ESR spectroscopy, in particular, for compounds containing the Fe—O—Fe fragment, was emphasised in a recent review¹⁴⁹ devoted to the synthesis and properties of binuclear iron complexes. Actually, some researchers believed^{163, 167} that solutions of the μ -oxo dimeric $\text{Pc}^{\text{t}}\text{Fe}$ complex are inactive for ESR spectroscopy both at room temperature and at 77 K.

The reaction of μ -oxo dimers of PcFe with nitrogen-containing compounds afforded μ -oxo dimeric complexes in the first stage. According to the hypotheses for the structures of the initial μ -oxo dimers, the structures $\text{LPcFe}^{\text{III}}\text{OFe}^{\text{III}}\text{PcL}$ (**5**),^{168, 169} $\text{H}_2(\text{LPcFe}^{\text{II}}\text{OFe}^{\text{II}}\text{PcL})$ or $(\text{LH})_2[\text{PcFe}^{\text{II}}\text{OFe}^{\text{II}}\text{Pc}]$ (**6**)^{6, 7, 56, 128, 152} were assigned to the above-mentioned complexes. Complete X-ray diffraction analysis of one of the complexes of this type ($\text{L} = \text{MeIm}$) demonstrated that the phthalocyanine ligands in this compound are located parallel to each other.⁴⁵ The Fe—N(MeIm) distance (2.039 Å) virtually coincides with that in the $\text{PcFe}(4\text{-MeC}_5\text{H}_4\text{N})_2$ complex (2.04 Å).⁴⁴ The Fe—O—Fe angle is 178.9° .⁴⁵ The structure of the axially coordinated μ -oxo dimeric PcFe complex exhibits two major distinctions from the structures of the well-characterised μ -oxo dimeric complexes of iron porphyrins without axial ligands:^{148–151} (1) central iron atoms lie virtually in the plane of the phthalocyanine ligand, which is in marked contrast to the structures of the porphyrin analogues in which the high-spin iron(III) ions deviate from the plane of the ligand by 0.3–0.5 Å;^{100, 148, 149} (2) coordination polyhedra about the central atoms are tetragonal bipyramids, whereas the coordination polyhedra in all μ -oxo dimeric iron complexes with macrocyclic ligands are tetragonal pyramids.^{148, 149} In studies^{45, 168} in which the structure **5** was assigned to the axially coordinated μ -dimeric PcFe complex, the first anomaly was attributed to the fact that this complex contains low-spin ($S = 1/2$; $S = 1/2$) rather than high-spin iron(III) ions.¹⁶⁸ The unusual coordination polyhedron was assigned to the 'unique' properties of this class of compounds.⁴⁵ However, it was noted¹²⁸ that the above-mentioned anomalies can be readily explained assuming that the central iron atoms in the μ -oxo dimeric PcFe complexes exist in oxidation state +2 (the structure **6**). Their electronic absorption spectra are typical of μ -oxo dimeric PcFe complexes with the parallel arrangement of the phthalocyanine ligands.⁶² Thus the Q band ($\lambda_{\text{max}} \approx 627 \text{ nm}$) is shifted hypsochromically compared to the Q band of monomeric PcFe complexes and its position depends only slightly on the nature of the axial ligand. The data on magnetic susceptibility and the parameters of the Mössbauer spectra of these compounds are given in Table 14. Note once again that all specimens occur (according to the data from Mössbauer spectroscopy) as mixtures of different coordination forms of PcFe,^{45, 168, 169} and, consequently, magnetic susceptibility data must be considered with caution. However, the parameters of the Mössbauer spectra most probably correspond to low-spin iron(II) complexes (see Tables 2 and 5) rather than to low-spin iron(III) complexes (see Table 10). The electric field gradient of the μ -oxo dimeric PcFe complex, which is axially coordinated by 4-MeC₅H₄N, has a positive sign.¹³⁴ Comparison of the Mössbauer spectra of the form 627 with the spectra of the oxo(1) and oxo(2) isomers suggests that the oxo(2) isomer and the axially coordinated μ -oxo dimeric complex are identical in geometry.

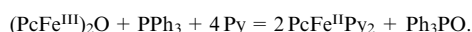
The chemical behaviour of the μ -oxo dimeric PcFe complexes was studied in detail with the aim of determining the valence state of the central iron atoms.^{6, 7, 56, 128, 152} The reactions of the initial μ -oxo dimeric form of both unsubstituted and substituted PcFe (the form 690) with nitrogen-containing heterocyclic com-

Table 14. Mössbauer spectra of the form 627 of the iron phthalocyanine complexes.¹⁶⁸

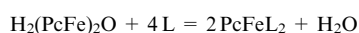
L	<i>T</i> / K	δ / mm s ^{−1}	ΔE_{Q} / mm s ^{−1}	$\mu_{\text{eff}} / \mu_{\text{B}}$
4-MeC ₅ H ₄ N	295	0.12	1.81	1.99
	77	0.19	1.75	—
	4.2	0.20	1.76	—
Pip	4.2	0.19	1.61	2.11
MeIm	4.2	0.17	1.58	2.16
Py	4.2	0.18	1.73	1.86

pounds^{6, 7, 128, 152, 168, 169} or isocyanides¹³⁵ afforded complexes with composition $\text{PcFe}^{\text{II}}\text{L}_2$ as the final products. On the assumption that the form 690 has the structure **3**, this reaction should be a redox process; however, oxidation products have never been detected. Therefore, the structure **4** is more probable for the form 690. The reactions of the form 690 of the $\text{Pc}^{\text{I}}\text{Fe}$ complex or its axially coordinated analogue (the form 627) with cyanide anions in organic solvents afforded the well-known $\text{Na}_2[\text{Pc}^{\text{I}}\text{Fe}(\text{CN})_2]$ complex.^{128, 167} The electronic absorption spectra for these reactions have distinct isosbestic points.

Data on the oxidation of triphenylphosphine with the μ -oxo dimer of PcFe (the form 690) under an inert atmosphere have been published.¹⁷⁰



The formation of Ph_3PO suggests the trivalent state of the central iron atoms in the initial compound. These results are in contradiction with those obtained in the study of the reaction of the form 690 with diphenylpicrylhydrazine under oxygen-free conditions.⁶ Thus it was found that the oxidation of diphenylpicrylhydrazine under strictly oxygen-free conditions did not occur at all. However, when a controlled amount of oxygen was introduced into a reactor, oxidation catalysed by the metal complex occurred. Moreover, it was demonstrated that the reaction of the form 690 with quinoline (which apparently contained an impurity of isoquinoline) yielded water (in an equimolar amount with respect to the initial form 690).^{6, 152}



This behaviour is consistent with the structure **4** for the form 690. However, it was mentioned^{154, 162} that when μ -oxo dimeric PcFe complexes were prepared by the reactions with O_2 , the oxygen was consumed in a ratio $\text{O}_2 : \text{PcFe} = 1 : 4$, and the only reaction product, *viz.*, the μ -oxo dimer, was formed in quantitative yield. This fact contradicts the structure $[\text{HPc}^{\text{R}}\text{Fe}]_2\text{O}$ (**4**), which can be formed from $\text{Pc}^{\text{R}}\text{Fe}$ and O_2 if a source of hydrogen atoms exists.

With the aim of refining the structure of the form 690, the reaction of $\text{Pc}^{\text{I}}\text{Fe}$ with oxygen in noncoordinating solvents (benzene and cyclohexane) was studied. It was found that: (1) the amount of oxygen consumed per mole of $\text{Pc}^{\text{I}}\text{Fe}$ introduced into the reaction depends on the concentration of the latter, and the $\text{O}_2 : \text{Pc}^{\text{I}}\text{Fe}$ ratio changes from 1 : 5.0 to 1 : 2.7 in the concentration range of $6.3 \times 10^{-3} - 1.1 \times 10^{-1} \text{ mol litre}^{-1}$; (2) the μ -oxo dimer is the major but not the only reaction product; the yield of this dimer varies from 78% to 95%. It was found that the reagents were consumed in side reactions, including oxidative destruction of the macrocycle by oxygen, which is strongly activated due to coordination in the complex with $\text{Pc}^{\text{I}}\text{Fe}$. Therefore, side oxidation reactions of the phthalocyanine macrocycle, substituents in this ring or other substrates can serve as a source of protons for the formation of the form 690.

The formation of the form 690 from the iron(III) derivative, *viz.*, $[\text{PcFe}(\text{OH})_2]^-$,^{128, 156} also calls for explanation. In our opinion, this process is accompanied by reduction of the iron atom with the hydroxide anion, which is one of the strongest reducing agents for PcFe complexes.¹⁷¹

Oxidation of the form 690 was examined for the first time in the study.⁷ The μ -oxo dimeric $\text{Pc}^{\text{I}}\text{Fe}$ complex (hereinafter, the form 630), which was prepared by the reactions of the form 690 with iodosobenzene or peracetic acid, was characterised by electronic absorption spectroscopy ($\lambda_{\text{max}} = 630 \text{ nm}$) and Mössbauer spectroscopy ($\delta = 0.58 \text{ mm s}^{-1}$, $\Delta E_{\text{Q}} = 0.34 \text{ mm s}^{-1}$ at 80 K). Later on, a procedure for the preparation of this compound was improved.¹²⁸ Thus this complex was prepared in virtually quantitative yield by the reaction of the form 690 with cumene hydroperoxide generated *in situ*. These authors were also the first to analyse the NMR spectra of the form 630. The reaction of the form 630 with cyanide anions afforded the known low-spin iron(III) complex, *viz.*, $\text{Na}[\text{Pc}^{\text{I}}\text{Fe}(\text{CN})_2]$,¹²⁸ which can be also

prepared by oxidation of the cyanide complex $\text{Na}_2[\text{Pc}^{\text{I}}\text{Fe}(\text{CN})_2]$ with bromine⁵⁵ or cumene hydroperoxide.¹²⁸ The reaction of the form 630 with hydrogen chloride yielded derivatives of iron(II) and (formally) iron(IV), *viz.*, hydrochloride $\text{Pc}^{\text{I}}\text{Fe} \cdot \text{HCl}$ and the radical cation $\text{Pc}^+ \cdot \text{FeCl}_2$, respectively.⁷ All the aforesaid provides evidence for the trivalent state of the central iron atoms in the form 630. Therefore, on the basis of the spectral data and the chemical properties of the μ -oxo dimeric PcFe complexes, the forms 690 and 627 were characterised as $\text{PcFe}(\text{II})$ derivatives and the form 630 was characterised as the μ -oxo dimer of iron(III) phthalocyanine.^{6, 7, 56, 128, 152, 163}

The reactions of PcFe with azides afforded μ -nitride PcFe complexes of the general formula $\text{PcFe}^{+3.5}\text{NFe}^{+3.5}\text{Pc}$ (Table 15).^{172–174} These compounds can be oxidised electrochemically or chemically to form complexes with composition $(\text{PcFe}^{+4}\text{NFe}^{+4}\text{Pc})^+ \text{X}^-$ (see Table 15).¹⁷² The structure of one of the resulting compounds, *viz.*, $[(\text{PcFe})_2\text{N}]\text{Br}$, was established by X-ray diffraction analysis.¹⁷⁵

Table 15. Parameters of Mössbauer spectra of the μ -nitrido and μ -carbido dimeric $\text{Pc}^{\text{R}}\text{Fe}$ complexes.^{172, 173}

Complex	$\delta / \text{mm s}^{-1}$	$\Delta E_{\text{Q}} / \text{mm s}^{-1}$
$(\text{PcFe})_2\text{N}$	0.06	1.76
$(\text{PcFe})_2\text{NPF}_6$	0.10	2.06
$(\text{PcFe})_2\text{C}$	−0.16	2.69
$[(4\text{-MeC}_5\text{H}_4\text{N})\text{PcFe}]_2\text{C}$	0.03	1.19
	0.12	0.25
$(\text{PyPcFe})_2\text{C}$	0.01	1.16
$(\text{PipPcFe})_2\text{C}$	0.01	1.11
$[(\text{MeIm})\text{PcFe}]_2\text{C}$	0.01	0.94
$[(4\text{-MeC}_5\text{H}_4\text{N})\text{PcFe}]_2\text{NPF}_6$	−0.10	1.76
$(\text{PyPcFe})_2\text{NPF}_6$	−0.09	1.76
$(\text{PipPcFe})_2\text{NPF}_6$	−0.09	1.73
$[(\text{MeIm})\text{PcFe}]_2\text{NPF}_6$	−0.09	1.52

Note. The spectra were recorded at 77 K relative to metallic iron.

The reaction of PcFe with tetraiodomethane in the presence of reducing agents, such as sodium dithionite or sodium borohydride, afforded μ -carbide PcFe complexes of the general formula $\text{PcFe}^{\text{IV}}\text{CFe}^{\text{IV}}\text{Pc}$ (see Table 15).^{176–179} This synthetic procedure has been improved quite recently, *viz.*, the reaction of $[\text{PcFe}^{\text{III}}(\text{OH})_2]^-$ with dichlorocarbene generated *in situ* was used.^{171, 180} Unfortunately, the poor quality of crystals of the $[(\text{MeIm})\text{PcFe}]_2\text{C}$ complex did not allow the researchers to perform a complete structure analysis of this complex.¹⁷⁸ However, the values of selected bond lengths and bond angles were determined. In particular, it was demonstrated that two phthalocyanine ligands in the complex are virtually parallel to each other (the $\text{Fe}-\text{C}-\text{Fe}$ angle is 178°).

Heterobimetallic oxo dimeric complexes of the PCrOFcPc type, where P is the dianion of α -substituted porphyrin, were synthesised and their properties were studied.¹⁸¹ These compounds were prepared by the reactions of $\text{PCr}^{\text{IV}}=\text{O}$ with PcFe . The synthesis, structures and properties of the μ -nitride heterodimer $(\text{TPP})\text{Fe}^{+3.5}\text{NFe}^{+3.5}\text{Pc}$, where TPP is tetraphenylporphin, as well as of its oxidised forms were described.¹⁸²

Among μ -oxo dimeric complexes of iron porphyrines, derivatives of tetra-*tert*-butyl-,⁶ octaphenyl-,¹⁴¹ octaethyl-⁵⁷ and octa(ethylthio)-substituted¹⁴³ porphyrines are presently available. All these compounds were characterised by electronic, IR and NMR spectra. The reaction of the pyridine adduct of iron octaphenylporphyrine with perchloric acid followed by the addition of HN_3 afforded the corresponding μ -nitride dimeric complex, which was characterised by electronic absorption, IR, Mössbauer and ESR spectra.¹⁸³ The pyridine monoadduct of this

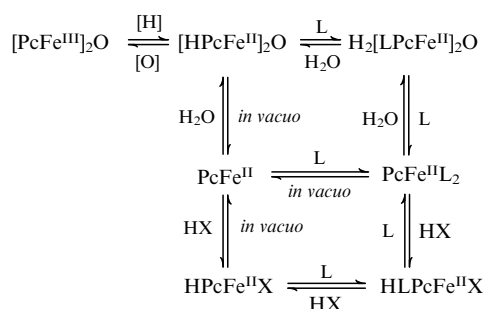
complex formed in frozen matrices adds reversibly one oxygen molecule per molecule of the initial complex.

Recently, the synthesis and selected properties of the heterobinuclear complex $\text{TAP}^{\text{Ph}}\text{Mn}=\text{NFeTAP}^{\text{Ph}}$ were reported.¹⁸⁴ However, the data from electronic absorption spectroscopy and mass spectrometry (primarily, the absence of the molecular ion and the $\text{TAP}^{\text{Ph}}\text{FeN}$ fragment) and the lack of Mössbauer spectra require that the suggested structure be considered with particular caution.

V. Some features of coordination chemistry of substituted iron phthalocyanines and their analogues

The interconversions of the coordination forms of iron phthalocyanines are shown in Scheme 2. As expected, the peripheral substituents in the macrocycle often break down these general regularities. Thus when bulky substituents (for example, the 2,4,6-trimethylphenyl substituents) were introduced at the α positions of the macrocycle, the μ -oxo dimeric Fe(II) and Fe(III) complexes were not formed at all due to steric hindrances caused by the substituents.^{7,8} In this case (under conditions of formation of μ -oxo dimeric complexes), the corresponding monomeric hydroxo complexes $\text{HPc}^{\text{R}}\text{Fe}(\text{OH})$ can be isolated. In an alkaline medium, the latter are converted into the corresponding oxoferryl derivatives, which undergo polymerisation upon prolonged storage.^{7,8}

Scheme 2



The effect of the electronic properties of substituents on the behaviour of iron phthalocyanines is generally manifested only in the relative stabilities of particular forms and in the positions of the bands in the electronic absorption spectra. The qualitative characteristic features of this effect can be observed only in special cases. For example, due to the presence of eight electron-withdrawing substituents, iron (3,5)-octakisnitrophthalocyanine^{7,8} reacts with nitrogen bases to give initially the $\text{PcFe}^{\text{II}}\text{L}_2$ complex, which is converted into the isoelectronic form $\text{Pc}^{3-}\text{Fe}^{\text{III}}\text{L}_2$ containing the stable phthalocyanine radical anion. Due to the presence of four SPH substituents in iron tetrakis(phenylthio)phthalocyanine, the iron ion has the $^3A_{2g}[(d_{xy})^2(d_{xz},d_{yz})^2(d_{z^2})^2]$ electronic configuration²⁷ rather than the $^3E_g[(d_{xy})^2(d_{xz},d_{yz})^3(d_{z^2})^1]$ configuration typical of $\text{Pc}^{\text{R}}\text{Fe}$. When eight electron-donating alkoxy groups are introduced into PcFe at positions adjacent to the macrocycle (at positions 1 and 4), the central iron atom is initially subjected to electrochemical oxidation, whereas the phthalocyanine ligands are oxidised in the complexes containing other substituents in the macrocycle.¹⁰⁹

VI. Major fields of application of iron phthalocyanines and their analogues

High catalytic activity of PcFe in decomposition of peroxides and in oxidation of some classes of organic compounds had been discovered by Cook^{185–187} back in the late 1930s. The use of iron phthalocyanines in catalysis has been expanded substantially since these years.^{3,188} Thus these compounds were used as homoge-

neous and heterogeneous catalysts of epoxidation of alkenes,^{188,189} oxidation of hydrocarbons to alcohols, aldehydes, quinones and ketones^{190–194} and oxidation of arylamines,¹⁹⁵ phosphines,^{162,196} thiols^{197–199} and conjugated aromatic systems.²⁰⁰ Electrodes modified with iron phthalocyanines and their analogues were used for electrooxidation of thiols,¹⁹⁷ electroreduction of molecular nitrogen to ammonia^{201,202} and electroreduction of carbon dioxide,²⁰³ sulfur dioxide,²⁰⁴ nitrogen oxides²⁰⁵ and molecular oxygen.^{206–208}

The chemo- and electrochromic properties of iron phthalocyanines and their analogues as well as variations in the conducting properties of these complexes depending on the medium made it possible to use these compounds in sensors for halogens,²⁰⁹ nitrogen oxides,²¹⁰ oxygen²¹¹ and aldehydes.²¹² Photochemical reactions of PcFe are well studied, which allows the use of this compound for the preparation of photosensitive materials (including those operating in the near IR region²¹³), photoconducting devices,²¹⁴ photosensitive inks²¹⁵ and materials for optical data recording and storage^{216,217} as well as for the production of high-contrast photographic materials.²¹⁸

Since axially coordinated complexes of iron phthalocyanines are readily available compounds, highly sensitive and selective membranes for gas separation²¹⁹ and food storage²²⁰ were constructed on the basis of these complexes. The use of cathodes modified with PcFe and its analogues in lithium cells with aggressive electrolytes, such as thionyl chloride and sulfur dioxide, made it possible to improve substantially their discharge characteristics.^{221–225} Intercalation of iron phthalocyanine into the structures of inorganic oxides leads to the appearance of magnetic properties in the resulting materials.²²⁶

In the reactions with reducing agents, such as ascorbic acid, catalysed by iron phthalocyanines, different so-called active oxygen forms (primarily, oxygen-centred radicals) are generated. This made it possible to initiate studies of complexes of iron phthalocyanines and their conjugates with proteins, DNA and RNA as potential drugs in catalytic (dark) therapy of cancer.^{21,227,228} In addition, high antihistamine and antiserotonin activities of PcFe derivatives were observed in a number of studies.^{5,229} The use of these compounds as deodorising agents is based on their high oxidase activity.²³⁰ Semiconducting properties of iron phthalocyanines and their analogues have received little use.^{9,13} Selective axial coordination of iron phthalocyanine to nitrogen-containing compounds allows one to solve a number of analytical problems by NMR spectroscopy.^{105–108}

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^f — *Kinet. Catal. (Engl. Transl.)*

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Fractal analysis of macromolecules

V U Novikov, G V Kozlov

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Abstract. Data on the fractal forms of macromolecules, the existence of which is predetermined by thermodynamic nonequilibrium and by the presence of deterministic order, are considered. The limitations of the concept of polymer fractal (macromolecular coil), of the Vilgis concept, and of the possibility of modelling in terms of the percolation theory and diffusion-limited irreversible aggregation are discussed. It is noted that not only macromolecular coils but also the segments of macromolecules between topological fixing points (cross-links, entanglements) are stochastic fractals; this is confirmed by the model of structure formation in a network polymer. The bibliography includes 141 references.

I. Introduction

The theory of fractals and its application to physical and chemical processes has been vigorously developing in recent years.^{1–8} To facilitate the understanding of the results presented in this review, we shall introduce some notions and definitions and consider briefly the grounds for applying the principles of synergetics and fractal analysis to the description of structures and properties of polymers.

Fractals are self-similar objects invariant with respect to local dilatations, *i.e.* objects that reproduce the same shape during observation at various magnifications. The concept of fractals as self-similar ensembles was introduced by Mandelbrot,¹ who defined a fractal as a set for which the Hausdorff–Besicovitch dimension always exceeds the topological dimension. The fractal dimension D of an object inserted in a d -dimensional Euclidean space varies from 1 to d . Fractal objects are the natural filling of the gap between known Euclidean objects with integer dimensions 0, 1, 2, 3... The majority of naturally existing objects proved to be fractal, which is the main reason for the vigorous development of the methods of fractal analysis.

According to the Family classification,⁹ fractal objects can be divided into two main types, namely, deterministic and statistical objects. Deterministic fractals are self-similar objects which can be precisely constructed on the basis of several fundamental laws.

Typical examples of these fractals are the Cantor set ('dust'), the Koch curve, the Sierpinski gasket, the Vicsek snowflake, *etc.* Two properties of deterministic fractals are most important, namely, the possibility of exact calculation of the fractal dimension and the infinite range of self-similarity ($-\infty$; $+\infty$). Since a line, a plane, or a volume can be divided into an infinite number of fragments in different ways, it is possible to construct an infinite number of deterministic fractals with different fractal dimensions. Therefore, deterministic fractals cannot be classified without introducing other parameters, apart from the fractal dimension.

Statistical fractals are generated by disordered (random) processes. An element of disorder is typical of most real physical phenomena and objects. The fact that disorder, *i.e.* the absence of any spatial correlation, is a sufficient condition for the formation of fractals was first noted by Mandelbrot.¹ A typical example of this type of fractal is the random-walk path. However, real physical systems are often inadequately described by purely statistical models. Among other reasons, this is due to the effect of excluded volume. The essence of this effect lies in the geometric restriction which forbids two different elements of a system to occupy the same volume in space. This restriction is to be taken into account in the corresponding modelling.^{10,11} The best-known examples of this type of models are self-avoiding random walk, 'lattice animals' and statistical percolation.

In a definite range of scales, fractals have different topological structures depending on the maximum number of elements connected with the given element of the system. If each element can be connected to not more than two other elements, the resulting structure has no branching. By analogy with linear polymers, Family⁹ has called these types of fractals linear fractals. If branching does occur, the resulting fractal has a framework structure; these types of fractals are referred to as branched fractals.

The microstructure of polymers can possess a high degree of self-ordering of either natural or artificial origin;¹² this represents one extreme case. The other extreme case is represented by chaos, which is the antithesis of order. Fractal analysis considers intermediate situations, *i.e.* those located between full order and full chaos. As a rule, these systems are obtained under conditions far from thermodynamic equilibrium; they fill the gap between periodic structures and fully disordered systems.¹³ In other words, fractal structures should possess a certain level of intermediate order. Therefore, when studying thermodynamically nonequilibrium solids (the class to which polymers normally belong¹⁴) possessing a local order,¹⁵ it is important to consider the relationship between the level of local order and the degree of fractality.

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At present, it is beyond doubt that the approximation of a real polymer by a continuous medium is inadequate.¹⁶ Even during the synthesis of polymers, numerous micro-, meso- and macro-defects arise; during performance, they can be further developed. Moreover, it has been found empirically that even those media that are initially homogeneous acquire upon deformation a hierarchical block structure, the characteristic dimensions of which L_i obey, with rather high accuracy, the relation

$$A_i = \frac{L_{i+1}}{L_i} = \text{const},$$

where A_i is the automodelling coefficient, $i = 0, 1, 2, \dots$ ^{3, 17, 18}

An important characteristic of structural elements of a solid is Euclidean dimension d , which can take on the following values: $d = 0$ implies point defects, $d = 1$ corresponds to linear defects (dislocations), $d = 2$ means planar defects (grain boundaries, twins, etc.), and $d = 3$ describes three-dimensional structures. The Euclidean dimension can characterise highly ordered symmetrical microstructures which do not often arise even in materials produced under quasi-equilibrium conditions. Nonequilibrium systems produced under essentially nonequilibrium conditions, which represent a sort of casts of dynamic dissipative structures, cannot at all be adequately described in terms of classical methods of metallography or radiography.^{17–21} This is even more so for solid (vitreous) polymers, which are, by definition, thermodynamically nonequilibrium systems. Indeed, the atomic structure of nonequilibrium materials can possess a quasicrystalline order, characterised by five-, seven-, thirteen- or higher-fold elements of symmetry²¹ forbidden by the Brouwer theorem, which underlies the classical techniques of X-ray diffraction analysis. Moreover, numerous fractographical^{4, 17, 21} and geophysical¹⁸ studies have revealed fractality of the structures of many materials and essentially non-Euclidean geometry of the deformation and the fracture of solids. Therefore, the traditional methods of the mechanics of continua, which are based on the assumption of homeomorphism of deformations, regarded as imaging of the body being deformed to the Euclidean space, are unable to describe adequately the rheological behaviour and fracture of real materials, in particular, polymers.

A significant breakthrough in tackling this problem is associated with the introduction into physicochemical analysis practice of the ideas and methods of synergetics[†] and fractal analysis.^{3, 5, 6, 8, 20, 21} In particular, it was shown that chaotic systems (amorphous phases, fractured surfaces, etc.) formed under nonequilibrium conditions which are totally disordered at first glance, actually display unusual elements of order.^{2, 20} Whereas crystals possess a certain symmetry and translational invariance, nonequilibrium systems can possess chirality even if they have no quasicrystalline structure³ and, what is the most important, these systems are scale invariant in a definite range of self-similarity.^{2, 3} Self-similarity is characterised quantitatively by the so-called Renyi dimension d_q . Unlike the topological dimension, it can be both an integer and a fraction¹ and is defined by the relations

$$d_q = \begin{cases} \lim_{\varepsilon \rightarrow \infty} \left[\frac{\ln \sum_{i=1}^M P_i^q(\varepsilon)}{(1-q)\ln \varepsilon} \right], & q \neq 1, \\ \lim_{\varepsilon \rightarrow \infty} \left[\frac{\ln \sum_{i=1}^M P_i(\varepsilon) \ln P_i(\varepsilon)}{\ln \varepsilon} \right], & q = 1, \end{cases}$$

where M is the minimum number of d -meric boxes with side ε needed to cover all the elements of a structure, $P_i(\varepsilon)$ is the

probability that a point of the structure belongs to an i th element of the bulk coverage ε^d , and q is the parameter of transformation of the measure ('magnification parameter').

For Euclidean objects (smooth curves or regular lattices in a plane or in a bulk, etc.), the following identity holds:¹⁶

$$d_q \equiv d, \text{ where } -\infty < q < \infty.$$

In the case of regular mathematical fractals such as the Cantor set, the Koch curves and Sierpinski gaskets constructed by recurrent procedures, the Renyi dimension d_q does not depend on q but¹⁶

$$d_q = d_H = \text{const} < d, \text{ } -\infty < q < \infty,$$

where d_H is the Hausdorff–Besicovitch dimension (Hausdorff dimension). According to the mathematical definition,⁴ the Hausdorff dimension d_H is a local characteristic of a set in the range of scales chosen, which can be covered by 'spheres' not necessarily having identical diameters, provided that the diameter of each sphere is smaller than a chosen diameter. The fractal dimension of the structure of a macromolecule d_f can be determined physically in the range of scales in which the structure elements are self-similar, i.e. when they are fractals. Since the ranges of d_f and d_H coincide, the $d_f = d_H$ is referred to as the fractal (Hausdorff) dimension of a macromolecule.

Natural fractals such as clouds, polymers, aerogels, porous media, dendrites, colloidal aggregates, cracks, fractured surfaces of solids, etc., possess only statistical self-similarity, which, furthermore, takes place only in a restricted range of sizes in space.^{1–4, 16} It has been shown experimentally for solid polymers²² that this range is from several angstroms to several tens of angstroms.

The relationship between the level of local order and the degree of fractality of disordered solids can be described using general mathematical terms.³ In particular, as regards the structure of solid polymers, it is noteworthy that the majority of researchers take for granted that segment-size structural associates are formed in polymers, although the particular type of packing in these associates is still debated.^{15, 23} It should be emphasised that the view on the amorphous state as being totally disordered is incorrect. According to the Ramsay theorem,³ any rather great number $i > R(i, j)$ of points or objects (in this particular case, structural elements) contain necessarily a highly ordered subsystem of $N_j \leq R(i, j)$ elements. Thus, no totally disordered systems (structures) exist. It can be shown in a similar way that any structure consisting of N elements, where $N_j > B_N(j)$, is a set comprising a finite number $k \leq j$ of self-similar structures embedded into one another and having, in the general case, different Hausdorff dimensions. This means that, irrespective of its physical nature, any system consisting of a relatively great number of elements is a multifractal (in a special case, monofractal) characterised by a spectrum of Renyi dimensions d_q , $q = -\infty$ to ∞ .³ The tendency of condensed systems to self-organisation into scale invariant multifractal forms is a consequence of fundamental principles of thermodynamics of open systems and d_q values are determined by the competition between short- and long-range interatomic interactions, which stipulate the volume compressibility and the shear rigidity of solids, respectively.²⁴ Since the physicochemical properties of polymers depend appreciably on the topology of the structure, the real polymer structures can be studied using the results of physical and mechanical measurements.^{25, 26}

Yet another important property of fractals which distinguishes them from traditional Euclidean objects is that at least three dimensions have to be determined, namely, d , the dimension of the enveloping Euclidean space, d_f , the fractal (Hausdorff) dimension, and d_s , the spectral (fracton) dimension, which characterises the object connectivity. [For Euclidean spaces, $d = d_f = d_s$; this allows Euclidean objects to be regarded as a specific ('degenerate') case of fractal objects. Below we shall repeatedly encounter this statement.]²⁷ This means that two

[†]Synergetics is an interdisciplinary field of knowledge dealing with identification of the general features of the processes of formation, stability and destruction of ordered time and space patterns in complex nonequilibrium systems of diverse natures.

fractal dimensions, d_f and d_s , are needed to describe the structure of a fractal object (for example, a polymer) even when the d value is fixed. This situation corresponds to the statement of nonequilibrium thermodynamics according to which at least two parameters of order are required to describe thermodynamically nonequilibrium solids (polymers), for which the Prigogine–Defay criterion is not met.^{28, 29}

In conclusion, we consider the relationship between the characteristics of percolation and fractal clusters. First of all, note that a percolation cluster near the percolation threshold is a fractal with a dimension of ~ 2.5 (for $d = 3$).^{7, 30, 31} This value can be easily derived from the known relationship between d and the critical percolation indices β and ν .^{9, 30} The relationships between the critical percolation indices β , ν and t and fractal dimension of a percolation cluster d_f have been reported⁷

$$\beta = \frac{1}{d_f}, \nu = \frac{2}{d_f}, t = \frac{4}{d_f}.$$

The critical indices estimated from these relations fall into the admissible ranges of variation — $\beta = 0.39–0.40$, $\nu = 0.8–0.9$, and $t = 1.6–1.8$, determined in terms of the percolation model for three-dimensional systems. The researchers⁷ noted that not only numerical values but also the meanings of these values coincide. Thus the index β characterises the chain structure of a percolation cluster. The $1/d_f$ value, which serves as the index of the first subset of the fractal percolation cluster in the model considered,⁷ also determines the chain structure of the cluster. The index ν is related to the cellular texture of the percolation cluster. The $2/d_f$ index of the second subset of the fractal percolation cluster is also associated with the cellular structure. By analogy, the index t defines the large-cellular skeleton of the fractal percolation cluster.[‡] Thus, these critical indices are universal and significant for analysis of complex systems, the behaviour of which can be interpreted in terms of the percolation theory.

It has been noted above that the structures and properties of polymers are studied using the principles of synergetics and methods of fractal analysis. This is based on several prerequisites. Firstly, amorphous glassy polymers have thermodynamically nonequilibrium structure.³² Schäfer and Keefer (see Ref. 10, p. 62) showed that fractal structures are formed in nonequilibrium processes. Therefore, there is good reason to believe that there are fractal structures in glassy polymers and that they can be described using the methods of synergetics. These assumptions have been repeatedly confirmed by experiments.^{32–39}

For example, the low-frequency region of the spectra of inelastic light scattering of amorphous polymers is a broad structureless plateau.²² This is due to the fractal structure of polymers on small linear scales.^{22, 35}

Fractal objects are characterised by the following relation between the mass M (or density ρ) and the linear scale of measurement L :³

$$M(L) \propto L^{d_m}, \quad (1)$$

where d_m is the mass scaling index.

Unlike mathematical fractals, real fractals (including polymers) have two natural scale lengths, $L_{\min}$ and $L_{\max}$ (Fig. 1); for lengths outside this range, the object is not a fractal.³ The lower limit $L_{\min}$ is related to the finite size of structural elements, while the upper limit $L_{\max}$ is associated with the tending to the limit of d_f . It has been found experimentally for polymers^{22, 35, 40} that $L_{\min}$ has an order of several angstroms and $L_{\max}$ is about several tens of angstroms. It is noteworthy that the same range of existence of a local order is typical of the cluster model in which the size (length)

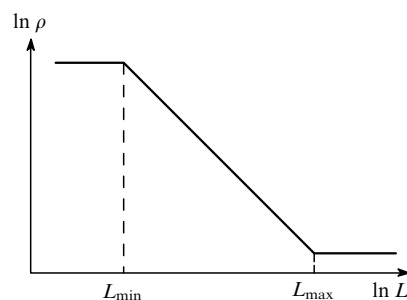


Figure 1. Density ρ vs. the length scale L of the real fractal. The range $L_{\min}–L_{\max}$ is the region of existence of the fractal.³

of a statistic segment l_{st} is the lower limit and the distance between the clusters R_{cl} is the upper limit.

It often turns out in studies of polymers that strictly derived relations describe adequately the behaviour of rubbers (*i.e.*, polymers at temperatures above the glass transition temperature T_g) but do not hold for the vitreous state. This is explained, first of all, by the sharp decrease in the mobility of chains below T_g or by ‘freezing’ of the structure.⁴¹ Strictly speaking, there is no fundamental difference between the molecular structure above and below T_g ; in both cases, the structure is formed by long-chain macromolecules. They differ in the fact that the thermodynamically unstable state of the polymer existing below T_g is replaced by a quasi-equilibrium state above T_g . Within the framework of fractal analysis, this means that the polymer structure ceases to be a fractal at $T \geq T_g$ and becomes Euclidean body (or, at least, a fairly close approximation). As noted by Flory,⁴² the ability to withstand severe deformations and restore entirely the initial characteristics when the stress has been relieved is a property exhibited, under appropriate conditions, by almost any polymer consisting of long-chain macromolecules. This feature is also manifested to some degree beyond the temperature range in which the ‘rubber elasticity’ phenomenon is observed. In other words, the macromolecular ‘essence’ of the polymer is more significant than the state in which the polymer occurs. Therefore, the use of the real (fractal) dimension of the object in the relations derived for rubbers⁴² is expected to provide fairly accurate results when applied to vitreous polymers.

Secondly, polymers are known to possess multilevel structures (molecular, topological, supermolecular, and floccular or block levels), the elements of which are interconnected.^{42, 43} In addition, an external action on a polymer can induce the formation of new (secondary) structural elements — cracks, fractured surfaces, plastic flow regions, *etc.* These primary and secondary structural elements as well as the processes forming them are characterised by miscellaneous parameters; therefore, only empirical correlations have been obtained, at best, between these parameters. If each of the above-mentioned elements (processes) is described by a standard parameter, for example, fractal dimension, one can derive analytical equations relating them to one another and containing no adjustable parameters. This is very significant for the computer synthesis of structure and for the prediction of properties and behaviour of polymeric materials during performance. Note that fractal analysis has been employed successfully to describe the phenomena of rubber elasticity^{16, 44, 45} and fluidity.^{25, 46–48}

Thirdly, legitimate application of these methods requires the use of a physically justified number of parameters describing the polymer structure. In this sense, the Euclidean and fractal objects are fundamentally different: the former require only one space dimension (Euclidean), whereas fractal objects (spaces) require not less than three dimensions.

Yet another important aspect is the change in the fractal dimension of polymers when they are simulated on fractal rather than Euclidean lattices. This fact is also important from the

‡ The relationship between the critical percolation indices and the fractal dimension of the percolation cluster for three-dimensional systems and examples of determination of these values for filled polymers are considered in more detail in the book cited.⁷

practical standpoint for multicomponent polymer systems. The introduction of a dispersed filler into a polymer matrix results in structure ‘perturbation’; in terms of fractal analysis, this is expressed as an increase in the fractal dimension of this structure. As shown by Novikov *et al.*,²⁵ the particles of a dispersed filler form in the polymer matrix a skeleton which possesses fractal (in the general case, multifractal) properties and has a fractal dimension. Thus, the formation of the structure of the polymer matrix in a filled polymer takes place in a fractal rather than Euclidean space; this accounts for the structure modifications of the polymer matrix in composites.

Proceeding from general statements, note that the term ‘multifractal’ can be understood in two ways as applied to polymers. It is shown below that the fractal dimension of a chain section between points of chemical cross-linking (or between physical entanglements) D is determined by the molecular mass of this section M_s (M_{en}) or by the cross-linking density v_s (or density of the entanglement network v_{en}). The M_s (M_{en}) value has a definite distribution;²⁷ hence, the dimension D would be characterised by a similar distribution.⁴⁹ Since the parameter D is uniquely related to the fractal dimension d_f of the supermolecular structure, d_f would be also characterised by a certain distribution. In other words, we are dealing with the distribution of fractal dimensions or multifractals. In addition, all the primary and secondary structural elements mentioned above are also multifractals; therefore, a polymer can be represented as a combination of elements having different weights, *i.e.*, again as a multifractal. Below we shall use averaged values of only the fractal dimensions of particular elements, at least as long as this approximation is useful for the understanding of the physical essence of the problem in question but does not decrease substantially the accuracy of estimates. Thus, the purpose of this review is to describe systematically the results obtained within the framework of fractal formalism and concerned with the studies of structure and properties of polymer macromolecules (linear, cross-linked, amorphous, *etc.*).

II. Modelling of macromolecules

1. Fractal dimension

The complexity of the polymer structure is reflected in the large number of dimensions needed to describe it. Alexander and Orbach²⁸ proposed the use of spectral or fracton dimension d_s for the description of the density of states on a fractal. The necessity of introducing d_s is due to the fact that the fractal dimension defined by Eqn (1) does not reflect this parameter. The investigators made use of the fact that anomalous diffusion of particles is expected on a fractal and, hence,

$$\langle r^2(t) \rangle \propto t^{2/(2+\delta)}, \quad (2)$$

where $r(t)$ is the distance covered by a diffusing particle in time t and δ is a scaling index for the diffusion constant. Having omitted the intermediate calculations, we present the final result obtained by Song and Roe¹⁴

$$d_s = \frac{2d_f}{2+\delta}. \quad (3)$$

The spectral dimension d_s is a true property of a fractal and is determined only by its connectivity. It differs from the mass scaling index [see Eqn (1)] or fractal dimension d_f and from the scaling index of the diffusion constant δ by the fact that it does not depend on the way in which a fractal has been inserted into the Euclidean space with dimension d . The dependence of d_s and δ on d_f is described by Eqn (3).

Alexander and Orbach²⁸ found that for a separate linear polymer chain, $d_s = 1$. In the case of a critical percolation cluster, the d_s value does not depend on d and amounts to $\sim 4/3$ (Table 1).

The dimensions of a linear macromolecule in different states have been considered.⁵⁰ The following states are known^{50–53} to be the most typical: 1 — compact globule, 2 — coil at the Θ -point, 3 — impermeable coil in a good solvent, 4 — permeable coil (the

Table 1. Values of d , d_s , d_f and δ for percolation clusters.²⁸

d	d_s	d_f	δ
2	1.36	1.9	0.80
3	1.42	2.5	1.55
4	1.39	3.3	2.71
5	1.44	3.8	3.30
∞	4/3	4.0	4.00

state typical of rigid-chain macromolecules), 5 — completely uncoiled rod-like macromolecule.

The radius of gyration of a macromolecule R_g depends on the molecular mass M and on the geometry of distribution of the molecule in space and is characterised by the scaling index ν (see Refs 32, 50).

$$R_g \propto M^\nu \quad (4)$$

From Eqns (1) and (4), it follows that²⁵

$$d_f = \frac{1}{\nu}. \quad (5)$$

Baranov *et al.*⁵⁰ introduced the dimension d_F , determined from the Flory formula⁵¹ for good solvents

$$d_F = \frac{3 - 2\nu_F}{\nu_F}. \quad (6)$$

The d_F value reflects the dimension of the sublattice in which the macromolecule is arranged, *i.e.*, it is a fractal dimension of the medium in which the molecule is located rather than of the molecule itself; d_F does not always coincide with the Euclidean dimension. The ν , d_f and d_F values of the three-dimensional space and the states of the macromolecule considered above are listed in Table 2.⁵² State 1 is encountered in globular proteins or on precipitation (below the Θ -point) of linear macromolecules from highly dilute solutions.^{53, 54} Conformation 5 is typical of some proteins or linear chains exposed to particular types of external action; conformations 2–4 are more trivial and fairly well studied.⁵¹ Analysis of the data of Table 2 leads to the conclusion that, for example, a macromolecular coil in the most frequently encountered states 2–4 is always a fractal (at $d = 3$).

Table 2. Values of ν , d_f , d_F (for $d = 3$) for various states of a macromolecule.⁵⁰

No.	State of macromolecule	ν	d_f	d_F
Poor solvent				
1	Globule	1/3	3	—
2	Coil at the Θ -point	1/2	2	—
Good solvent				
3	Coil	3/5	5/3	3
4	Permeable coil	2/3	3/2	2.5
5	Uncoiled chain	1	1	1

2. Polymer fractal

Cates⁵⁵ introduced the notion ‘polymer fractal’ by replacing the rigid bonds in a percolation cluster by flexible (phantom) links. This model can be used to describe the gelation process (Fig. 2).⁵⁶ Within the framework of this approach, Cates⁵⁵ described variations of the structure and the dynamics of dilute solutions of polymers. This approach is based on the following main ideas.

The replacement of rigid bonds in a percolation cluster by long phantom chains does not change the connectivity of a fractal (therefore, additional contacts between chains are regarded as

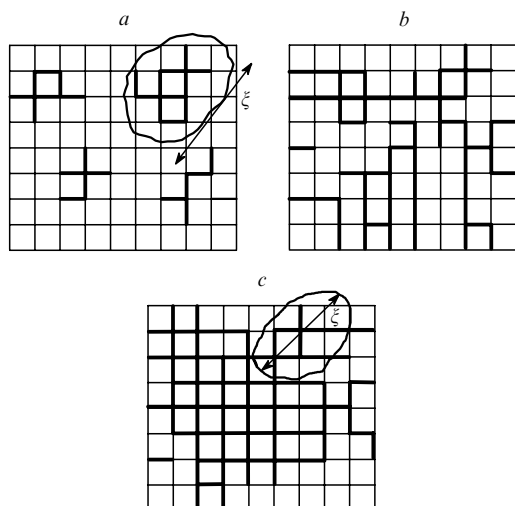


Figure 2. Scheme of the percolation of bonds during gelation:⁵⁶ (a) pre-gel state, (b) gelation point, (c) post-gel state; ξ is the characteristic linear scale.

imaginary) but does influence the dimension and the dynamic properties of the object. To describe the changes, at least three fractal dimensions are required.²⁸ The dimension of the initial fractal (in the percolation lattice) is determined by the fractal dimension d_{f0} using a mass scaling relation similar to (1).⁵⁷ The subscript 0 corresponds to the initial fractal with rigid bonds.⁵⁵ The dynamic properties can be studied using the spectral dimension d_s or (which is equivalent) using random walkers (the dimension d_w) arranged on a fractal. The latter version implies a scaling law for the root-mean-square displacement r [see Eqn (2)] of a random walker on a fractal in a time t ⁵⁶

$$r^{d_{w0}} \propto t, \quad (7)$$

where d_{w0} is the random-walk dimension at $d = 2$.

The case where $d_{w0} = 2$ corresponds to the classical Einstein diffusion. The r value is expressed in Euclidean distances; the process with $d_{w0} > 2$ is usually referred to as slow anomalous diffusion. The density of states is determined by the dimension d_s

$$d_s = \frac{2d_{f0}}{d_{w0}}. \quad (8)$$

It has been noted above that d_s is a true parameter of a fractal determined completely by the object connectivity. The replacement of rigid bonds by flexible links in a percolation cluster does not change d_s , i.e. in the Cates procedure,⁵⁵ d_s is an invariant value. However, the fractal dimension d_f and the walk dimension d_w change upon execution of this procedure. By using the 'Einstein correlation' relating the scaling indices of a fractal (in this case, d_f is used as the index) to the resistivity (a component of viscosity) $\bar{\xi}$, it can be shown^{55, 58} that for polymers with phantom bonds (i.e. for polymers with no excluded volume, for which $\bar{\xi} = 2$) the d_w value can be represented by the sum

$$d_w = d_f + 2. \quad (9)$$

Cates showed⁵⁵ that relation (9) is also valid for structures containing loops. In the case of an ideal polymer fractal with Gaussian chains and the connectivity parameter d_l , the fractal dimension d_f of a percolation cluster with phantom bonds can be expressed as follows:

$$d_f = \frac{2d_l}{2 - d_l}. \quad (9a)$$

For $d_l = 1$ (linear chains), Eqn (9a) provides the correct value, $d_f = 2$, corresponding to a macromolecular coil at the Θ -point (see Table 2). As noted above, $d_s = 4/3$ for a percolation cluster

irrespective of the dimension of the Euclidean space (see Table 1); therefore, from Eqn (9a), we obtain $d_f = 4$, which is consistent with the Flory–Stockmayer theory⁵⁹ for phantom chains. For three-dimensional space, $d_f > 3$ has no physical meaning because the object cannot be packed more densely than an object having Euclidean dimension. It is evident that this discrepancy is due to the phantom nature of the polymer chains postulated by Cates;⁵⁵ it is necessary to take into account self-interactions of chains due to which the dimension of a polymer fractal assumes a value which has a physical meaning.

In Eqn (9a), d_f has the same meaning as the fractal dimension of phantom Gaussian chains; therefore, the standard mean-field theory, taking account of the factor of excluded volume, can be applied to a polymer fractal.⁵⁶

The Flory approach can be used as the first approximation for this purpose.⁵⁹ In this case, the free energy F of an object with self-interactions can be represented by the sum⁵²

$$F = \left(\frac{R}{R_0}\right)^2 + v_u \frac{M^2}{R^d}, \quad (10)$$

where R is the size of a real fractal, R_0 is the size of an ideal phantom fractal without allowance for the interactions of excluded volume, v_u is an excluded volume parameter, M is the total mass of the fractal ($R_0^D \propto M$), and d is the dimension of the Euclidean space in which the fractal has been inserted. The first term in Eqn (10) is the elastic (or entropic) component of the free energy and the second term takes into account the volume interactions in terms of the mean-field theory.^{52, 59}

By minimising the free energy with respect to R , one can find the fractal dimension D of a swollen fractal, which is determined by the equation

$$D = \frac{d_s(d+2)}{d_s+2}. \quad (10a)$$

In the case of percolation clusters, Eqn (10a) gives $D = 2$ for $d_s = 4/3$ and $d = 3$ (see Ref. 56), while for linear polymers, $D = 5/3$ for $d_s = 1$ and $d = 3$ (see Ref. 60), which corresponds to an impermeable coil in a good solvent (see Table 2, state 3). The resulting dimensions are typical of macromolecular coils in monomeric solvents. Using the concept of polymer fractal, one can answer the question of what would happen if the monomeric solvent is replaced by a polymeric one, i.e., whether the polymer clusters and the clusters of a high-molecular-mass 'solvent' would be separated from one another or 'entangled'. This question can be answered by virtue of the equation⁶⁰

$$N = R_g^{D_1+D_2-d}, \quad (10b)$$

where N is the number of intersections of two arbitrary fractals with dimensions D_1 and D_2 .

The final relations for the dimensions of systems involving mixtures of polymer fractals (fractals in low- and high-molecular-mass solvents, melts of identical and arbitrary fractals) are given in Table 3.⁶⁰

The problems of penetration of polymers with arbitrary connectivity into confined spaces (for examples, pores or slits) have been discussed.⁶¹ It has been noted that the Flory theory, the blob model⁶¹ and the scaling concept provide identical results for linear chains; however, in the case of branched polymers, the Flory theory and scaling can lead to contradictory results when applied without invoking additional information.

For branched (and, hence, for cross-linked) polymers, the equation for the index ν in relation (4) has the form⁶¹

$$\nu = \frac{d_s+2}{d+2}, \quad (11)$$

and the fractal dimension D is determined by the ratio

$$D = \frac{d_s}{\nu}. \quad (12)$$

Table 3. Final relations for the dimensions of systems comprising mixtures of polymer fractals.⁶⁰

Parameter	Mono- meric- solvent $\delta_s = \delta_f = 0$	Poly- meric solvent $\delta_s = 1,$ $d_f = 2$	Melt of identical fractals $\delta_s = d_s,$ $\delta_f = d_f$	Melt of arbitrary fractals
Fractal dimension				
in terms of d_s	$\frac{d_s(d+2)}{d_s+2}$	$\frac{d+2}{2}$	$\frac{d_s(d+2)}{2}$	$\frac{d_s(d+1)(2-\delta_s)}{2(2+d_s-2)}$
in terms of d_f	$\frac{d+2}{2(1+1/d_f)}$	$\frac{d+2}{2}$	$\frac{d+2}{2+1/d_f}$	$\frac{d+2}{2-(\delta_f-2)/d_f}$
Saturation condition ^a	—	$d \leq 2$	$d_s \geq \frac{2d}{d+2}$	$\delta_f \geq 2 + \frac{d_f(d-1)}{d}$

Note. The δ_s and δ_f values are the spectral and fractal dimensions of the interglobular space in a solvent.

^a Transition from fractal to non-fractal behaviour.

Equation (5) is a special case of Eqn (12) for linear chains ($d_s = 1$).

In order to avoid the use of values such as the connectivity parameter (or chemical dimension) d_l or spectral dimension d_s , Lhuillier⁶² proposed a d -independent universal index r in the dependence

$$R_{g \max} \propto N_m^r, \quad (13)$$

where $R_{g \max}$ is the maximum radius of gyration of a macromolecular coil and N_m is the number of base units (monomers) in the chain.

The r value is supposed to vary in the range $1/d \leq r \leq 1$. It is believed that the r -fractals thus introduced provide a simple description for real polymers: $r = 1$ for linear chains and $r = 3/4$ for branched chains. However, Vilgis⁶³ have found that, in essence, the following relation holds:

$$r^{-1} = d_s; \quad (14)$$

this, in turn, implies that r -fractals can be reduced to polymer fractals, postulated by Cates.⁵⁵

A study by Stepleton *et al.*⁶⁴ was among the first which confirmed experimentally the fractal nature of a polymer chain taking a protein as an example. In a study of a frozen aqueous solution of a hemoprotein by electron spin relaxation, its fractal dimension was estimated to be 1.65 ± 0.004 . In the opinion of the researchers, this value is in good agreement with the fractal dimension of a self-avoiding random walk, which is equal to $5/3$.⁵⁷ This conclusion was drawn using the equation for the phonon density of states $\rho(\omega)$

$$\rho(\omega) \propto \omega^{d_s-1},$$

where ω is frequency.

It has been suggested^{64,65} that the exponent in the equation for $\rho(\omega)$ is determined by the fractal dimension. However, Alexander and Orbach²⁸ showed that in this case, the spectral dimension d_s is involved, which is not equal to d_f [see Eqn (8) and Table 1]. Note that the publication by Stepleton *et al.*⁶⁴ appeared earlier than the study by Alexander and Orbach.²⁸ In the case of self-avoiding random walk, $d_s = 1$; substitution of this value into the equation for $\rho(\omega)$ gives a result which, as shown by Young (see Ref. 10, p. 168), is at variance with experimental results.

Attempts to resolve this contradiction have been undertaken.^{66,67} Maritan and Stella (see Ref. 10, p. 151) calculated the fractal dimensions for 50 proteins using two methods. In one method, fractal dimension is a scaling index for the contour length of a macromolecule with respect to the distance between its ends

(it is equal to 1.19–1.82), while in the other method, the fractal dimension is a scaling index for the total mass with respect to the length, which is equal to 1.62–2.24. The calculations were performed using X-ray diffraction crystallographic parameters of proteins.

In our opinion, the results obtained for proteins^{64,65} do not appear contradictory. Undoubtedly, the fractal dimension presented in the study⁶⁴ is the spectral dimension d_s . Its value ($d_s = 1.65$) does not seem too great either, if one takes into account that the values $d_s = 1.65$ –1.80 were obtained for block poly(methyl methacrylate).³⁵ These large values of spectral dimension can be due to several reasons, first of all, to the high connectivity of the polymer chain.²⁸

In addition, the polymer chain cannot be modelled by self-avoiding random walk, as has been done by Young. Finally, Cappelli *et al.* (see Ref. 10, p. 156) demonstrated that the effective d_s value can be influenced by the non-homogeneity of block specimens, for example, porosity or inter-grain boundaries.

The difference between the d_l and d_f values found by Colvin and Stepleton⁶⁵ can also be easily explained. Indeed, d_l is a chemical dimension, as follows from the way of its determination,²⁷ d_f is the Hausdorff dimension. These values do not necessarily coincide. By using Eqn (10a) for a fractal swollen in a monomeric solvent, we obtain $D \approx 2.26$ for $d_s = 1.65$ and $d = 3$, which is in good agreement with both experimental data and the limiting D value for branched polymers.⁹

The following relation has been proposed:⁶²

$$d_l = \frac{d_f}{z}, \quad (15)$$

where

$$z = \frac{4+3D}{8}, \text{ for } 4/3 < D < 4. \quad (16)$$

When $D \approx 2.26$, the parameters z and d_l are 1.348 and 1.68, respectively, which is consistent with the estimate made by Colvin and Stepleton.⁶⁵ Calculation by an equation similar to (8) gives $d_w \approx 2.74$, *i.e.* slow anomalous diffusion on the fractal takes place.^{28,56}

The following expression relating d_w to d_l has been proposed:³¹

$$d_w = d_f \left(1 + \frac{1}{d_l} \right). \quad (17)$$

Assuming that $d_w = 3.37$ ('lattice animals'³¹), we obtain $d_l = 0.93$ –1.98. This interval agrees with the range of d_l found experimentally.⁶⁵

Thus, there are no contradictions suggested by Young between the estimates made in the two studies cited above^{64,65} but the large number of fractal dimensions used to describe the polymer structure creates certain difficulties. This is not a matter of principle because the dimensions considered above are interrelated.^{28,55,56,60–63,68–71}

3. Statistical fractal

Family⁹ considered the conformations of statistical branched fractals (which simulate branched polymers) formed in equilibrium processes in terms of the Flory theory. Using this approach, he found only three different states of statistical fractals, which were called uncoiled, compensated, and collapsed states. In particular, it was found that in thermally induced phase transitions, clusters occur in the compensated state and have nearly equal fractal dimensions (~ 2.5). Recall that the value $d_f = 2.5$ in polymers corresponds to the gelation point; this allows gelation to be classified as a critical phenomenon.

The fractal dimension of purely statistical models, *i.e.* models without the effect of excluded volume, can be determined accurately [see Eqn (9a)]. For linear polymers, this model corresponds to phantom random walk. In the case of branched statistical fractals, the corresponding model is a statistical branched cluster,

whose branching obeys the random-walk statistics. Since the root-mean-square distance between the random-walk ends is proportional to the number of walk steps N , then $D = 2$ irrespective of the space dimension. These types of structures have been studied.^{60, 72–74} The value $D = 4$ irrespective of d was obtained for a branched fractal. Unlike ‘ideal’ statistical models, models with excluded volume, *i.e.* those involving correlations, cannot be accurately solved in the general case. The D_f values for these systems are usually found either using numerical methods such as the Monte Carlo method or taking into account the spatial position of a re-normalisation group.

What are the physical conditions under which a statistical fractal has the most branched structure? It is clear that, when a large number of clusters are present in the system, they all occupy the available volume. The presence of other clusters restricts the degree of branching of each cluster; a cluster is more branched in the isolated state than in a concentrated solution. For polymer coils, this is expressed as an increase in D from its value in a dilute solution in a good solvent to the value at the Θ -point in concentrated solutions.⁷⁰

Yet another factor which also influences the shape of the cluster is whether or not attractive interactions are present. As the temperature increases, the attractive interactions diminish. For example, no interactions of this sort are found in isolated macromolecular coils in good solvents at high temperatures.⁷⁴ Family⁹ defined this state of a statistical fractal as an uncoiled state because in this case, it is characterised by the smallest fractal dimension.

Then Family used the version of the Flory theory proposed by Isaacson and Lubensky⁷⁵ for determination of the fractal dimension of an isolated statistical cluster. The method is based on the determination of the most probable cluster conformation using the free energy of repulsion. Under the influence of elastic free energy, the radius of the real cluster ‘tends’ to the radius of the ideal cluster which involves no repulsive interaction. After minimisation of the total free energy, the D_f value for an uncoiled cluster can be found from the expression

$$D = \frac{2(d+2)}{5}, \quad (18)$$

which was first obtained by Isaacson and Lubensky⁷⁵ for branched polymers in dilute solutions.

Equation (18) has two peculiar features: firstly, D depends appreciably on d and, secondly, there exists a critical dimension of Euclidean space $d_c = 8$ for which $D = 4$ in accordance with the ideal statistical model, *i.e.* the model without correlations. At $d_c > 8$, the correlations caused by the effect of excluded volume are no longer significant and D_f does not change. The value $d_c = 8$ was found in studies of branched polymers and ‘lattice animals’.⁷⁶ Calculations by formula (18) are in good agreement with the known results for ‘lattice animals.’

To elucidate the effects which increase D , Family considered conformations of one big cluster comprising N particles in the presence of other clusters with a size distribution. The large cluster does not ‘feel’ the presence of other clusters as long as their average diameter is small compared to its diameter. On the scale of lengths much greater than the radius of an average cluster, the big cluster interacts only with clusters similar to itself. It was found for polymers that, as the sizes of other clusters increase, they start to screen the effect of excluded volume, which is effective in the big cluster. The screening can change the fractal dimension of this cluster.

The best examples of processes with a cluster distribution are percolation and thermal critical phenomena, which are reflected, for example, by the Ising, Potts, and other models. Under equilibrium conditions in a system consisting of clusters with a size distribution, the average cluster size deviates in the vicinity of the critical point.

The state of a statistical fractal in which the excluded volume effect is compensated by the screening effect is referred to as the compensated state. For this state, Family has found that

$$D = \frac{d+2}{2}. \quad (19)$$

This expression is expected to be valid for any statistical critical cluster in the presence of clusters having a size distribution. The upper critical dimension for critical clusters can be determined assuming that in Eqn (19), $D = 4$. The result thus obtained, $d_c = 6$, is in good agreement with the data for percolation.⁷⁵

The above results confirm that the presence of numerous clusters and the deviation of the mean cluster size near the critical point results in the screening of the critical volume effect and in an increase in D . Another way of decreasing the repulsive interactions is to enhance the attractive interactions between the elements of an isolated cluster. In the general form, the free repulsive energy can be represented as a power series with respect to density with virial coefficients $w_2, w_3, \dots$, which describe the effects of interaction between pairs, triplets, *etc.*⁷⁷ The first term (with w_2) in this power series predominates. However, in the presence of attractive interactions, the second virial coefficient w_2 tends to zero and the term with w_3 should be taken into account. When $w_2 \rightarrow 0$, the polymer occurs in the vicinity of the Θ -point.⁷⁴ In this case, with minimisation of the total free energy with respect to R

$$D = \frac{4(d+1)}{7}. \quad (20)$$

This relation was first obtained by Bantle⁷⁸ for the conformation of an isolated branched polymer at the Θ -point. Calculation in terms of Eqn (20) for $D = 4$ gives $d_c = 6$, as for the compensated state.

Thus, the fractal dimension D increases near the compensation point; this is due either to the geometric screening of the excluded volume effect or to the enhancement of the attractive interaction. Big clusters near the critical point in thermally induced phase transitions and polymers at the Θ -point are examples of statistical fractals in the compensated state.⁹

Study of the conformation of a statistical fractal in a system occurring below the critical point and in the isolated state at $w_2 < 0$ showed that the fractal is very compact and has a globular conformation in both cases. This state of a fractal was called collapsed, by analogy with the collapsed state of polymers.

The conformation of clusters under these conditions was determined using the approach proposed⁷⁷ for studying the conformation of a branched polymer in a monodisperse melt, *i.e.* in a solution of coils with identical sizes. In the case of minimisation of the free energy with respect to R ,

$$D = d \quad (21)$$

For a purely statistical fractal for which $D = 4$, we obtain $d_{st} = 4$. This means that this type of statistical cluster is compact up to $d = 4$. Therefore, Family⁹ called this state of statistical fractals the collapsed state.

In the case of an isolated fractal, attractive interactions predominate below the compensation point; the second virial coefficient w_2 is negative and cannot be neglected in the power series mentioned above. The conformation of a fractal is determined by the balance between the first two terms in this series. The results are identical to Eqn (21) for $d_{st} = 4$. Thus, the conformation of an isolated statistical fractal below the compensation point is the same as the conformation of a big cluster below the critical point.

4. Experimental determination of fractal dimensions

Let us consider several experimental estimates of various fractal dimensions for polymers with allowance for the above theoretical statements. The index ν in Eqn (4) has been determined by small-angle neutron scattering for epoxy polymers;⁷⁸ it was found that

$\nu = 0.6$. It has been suggested⁷⁹ that so great a ν value is due to the enhanced chain rigidity of epoxy polymers. However, the use of Eqn (11) with $d_s = 4/3$ and $d = 3$ gives $\nu = 0.666$, which is close to the experimental ν value (see Table 2, the permeable coil model). Calculation using Eqn (12) for $d_s = 4/3$ and $\nu = 0.6$ gives $D \approx 2.22$, which is close to the fractal dimension for the compensated state of branched polymers in accordance with Eqn (20).

Silicate gels and epoxy polymers have been studied by Raman light scattering.^{34, 79} The spectral dimension d_s of silicate gels falls within the range from 1.11 to 1.43, depending on the method of calculation, which is consistent with the conclusion drawn by Alexander and Orbach.²⁸ The results of estimates of d_s from the data of Raman scattering and small-angle neutron scattering for two epoxy polymers with cross-linking densities differing by a factor of two and for the monomer used to prepare these epoxy polymers are presented in Table 4. Attention is drawn to the fact that the d_s values for all the three specimens are virtually equal [if the inaccuracy of determination of d_s is taken to be ± 0.05 (see Ref. 35)], the slight difference being due rather to the determination method used.

Table 4. Value of d_s for the DGEBA monomer^a and for epoxy polymers based on it determined by Raman light scattering (I) and small-angle neutron scattering (II) methods.⁷⁹

Example	I	II
DGEBA EDA ^b 1X	1.37	1.44
DGEBA EDA ^b 2X	1.33	1.44
DGEBA	1.32	1.52

^a Diglycidyl ester of bisphenol A. ^b Ethylenediamine.

The results of investigation of the transfer of energy between molecules acting as electron density donors and acceptors have been reported.^{80, 81} The Raman scattering method gives actually the fractal dimension of the surface on which the energy transfer takes place.⁸¹ The fractal dimensions found for silicates are in the range of 2.23–2.82;⁸¹ that for a polystyrene film is 2.2.⁸⁰

Cappelli *et al.* (see Ref. 10, p. 156) have studied the annihilation of the triplet excitons in naphthalene aggregates located in the pores of various materials including polymers. A common feature of these systems is non-classical annihilation kinetics, which resemble the annihilation kinetics of fractals. The coefficient of the annihilation rate k_a varies with time t

$$k_a \propto t^{-h}, \quad (22)$$

where h is the non-homogeneity index ($0 < h < 1$), which is equal to zero only for homogeneous specimens. The effective spectral dimension of the medium d'_s is given by the relation⁷⁰

$$d'_s = 2(1 - h). \quad (23)$$

The d'_s values for several polymers are listed in Table 5.

Cappelli *et al.*¹⁰ also measured h as a function of temperature. At low temperatures, all the studied polymers exhibit properties similar to the properties of fractals. As the temperature increases, h decreases, i.e. the d'_s value increases. In some specimens, $h \rightarrow 0$

Table 5. Effective spectral dimensions d'_s for some polymers.¹⁰

Polymer	Pore size μm	T/K	h	d'_s
Acetate A8	0.2	4	0.16	1.2–1.7
Acetate A1	0.1	4	0.47	0.8–1.1
Acetate A3	1.2	4	0.44	0.9–1.1
Nylon B214	0.2	4	0.21	1.2–1.6
Poly(methyl methacrylate)	—	77	0.1	1.8

as the temperature is raised. This implies that all the effects described by fractional dimensions are associated with disorder.⁸² A number of specimens behave as fractals also at room temperature. It is noteworthy that the d'_s values for the polymers studied vary over wide limits, from 0.8 to 1.8. In the case of poly(methyl methacrylate), d'_s exactly corresponds to the spectral dimension determined by Raman scattering measurements;^{22, 34} it is ~ 1.8 in both cases.

The theoretical concepts outlined above are confirmed rather accurately by experimental data. Nevertheless, it is worth noting that the concept of polymeric (macromolecular) fractal⁵⁵ has been developed for polymer solutions, while the Vilgis theory^{60, 61} is applicable only to rubbers and polymer melts, although it has been developed for condensed media. Therefore, it can be expected that extension of these concepts to the vitreous state of polymers would require some corrections taking into account the specific features of this state.

Some possible approximations have been considered by Cates,⁵⁵ who concentrated attention on macromolecular entanglements, which play an important role in the description of the behaviour of block polymers.^{83–86} Cates believes that the fact that the concept of polymer fractal neglects the effects of macromolecular entanglements is the main drawback of this theory. Nevertheless, Cates⁵⁵ introduced several simplifications which make it possible to ignore these effects for dilute solutions and relatively low molecular masses. However, in the opinion of Cates, even in the case of predominant influence of entanglements, theoretical interpretation of this phenomenon is impossible without preliminary investigation of the properties of the system in terms of Rouse–Zimm dynamics, which can serve as the basis for a more complex theory. It was assumed⁵⁵ that the effects of entanglement can be due to the substantially enhanced local friction of macromolecules.

5. Levels of fractality

Polymers exhibit the fractality inherent in them at different structural levels; both primary and secondary structural elements can be fractals. For example, macromolecular coils in Θ or in good solvents with $d_f \approx 1.66$ (with the Euclidean dimension $d = 3$) are fractals.^{1, 29} The fractality of a polymer at the molecular level can be demonstrated as follows. Lebedev⁸⁷ reported data on the change in the radius of gyration R_g of the macromolecules of block polystyrene, poly(methyl methacrylate) and polyethylene with the molecular mass M_w . The R_g value is related to the length of a macromolecule L_w in the following way:⁸⁸

$$L_w \propto R_g^{d_f}. \quad (24)$$

The length of a macromolecule can be determined from the known M_w , the molecular mass of one unit m_0 , and the projection of the bond length l_0 on the macromolecular axis using the simple dependence

$$L_w = \frac{M_w l_0}{m_0}. \quad (25)$$

The m_0 and l_0 values for the polymers mentioned above were taken from Ref. 89 and Ref. 90, respectively.

Figure 3a shows the variation of L_w vs. R_g . Taking account of this dependence, it was found that $d_f \approx 1.60$, which is close to the corresponding value for a macromolecular coil in a Θ -solvent ($d_f \approx 1.66$, see Table 2). The elements of Koch figures (Fig. 3b) resemble most closely the freely jointed chain model, which is normally used to simulate macromolecules.⁹¹ For this version, $d_f = 1.61$. Thus, the fractality of a block polymer at a molecular level can be regarded as proven.

The cluster model of the structure of amorphous polymers (Fig. 4) provides a quantitative description of supermolecular (supersegmental) structures in this type of polymer. The cluster with chains protruding from it ('interpenetrating' molecules) assumed in this model resembles the well-known cluster used in

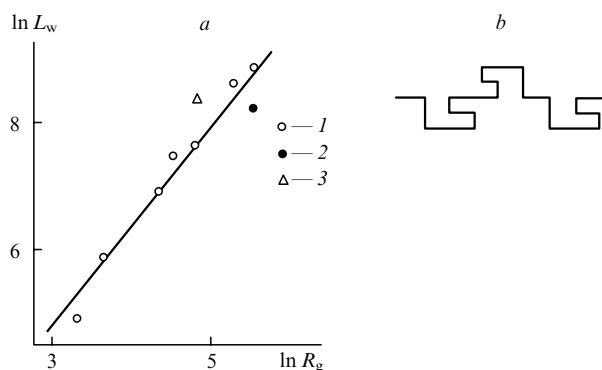


Figure 3. Chain length L_w vs. the radius of gyration R_g for a macromolecular coil of polystyrene (1), poly(methyl methacrylate) (2) and polyethylene (3) (a) and a variant of elements of the Koch curves having $d_f = 1.61$ (b).⁸⁸

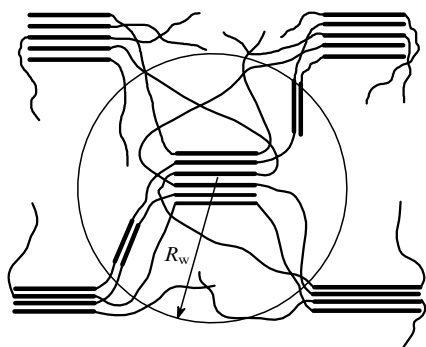


Figure 4. Cluster model of the structure of an amorphous polymer.

the Witten–Sander (WS) model.^{77,78} Such a cluster distinguished in a polymer bulk restricted by the radius R_w would possess at least two features typical of fractal clusters. One feature is self-similarity, caused by the presence of unstable clusters consisting of fewer segments than thermodynamically stable clusters (Fig. 4 shows them consisting of two segments). The other feature is that the density of particles (statistical segments) comprising the cluster would decrease on moving away from the cluster centre and thus stipulate the $\rho(L)$ dependence typical of fractals (see Fig. 1). In conformity with this dependence, it is assumed that the structure of an amorphous polymer contains sorts of ‘thickened’ and ‘rarefied’ sections. This ‘thickening’ of the material can be explained by assuming the existence of a local order (as opposed to the model of interpenetrating macromolecular coils, *i.e.*, the ‘felt’ model, proposed by Flory).^{92,93} Thus, the fractality of the structure of amorphous polymers in the ~ 0.3 – 5.0 nm range, shown experimentally in a number of studies,^{22,35} is confirmed indirectly by the presence of local order.

The size of a fractal cluster R_w and the number of particles in it N_r are related to each other by the following expression:⁸⁸

$$N_r \propto R_w^{d_f}. \quad (26)$$

Let us consider the procedure for estimation of the N_r and R_w values in terms of the cluster model.^{15,86} A cluster is regarded as a multifunctional unit in a fluctuation network of macromolecular entanglements; therefore, according to Flory,⁴² the reduced molecular mass M per cluster is estimated from Eqn (4). By dividing M into the molecular mass of a statistical segment, we obtain the number of particles (statistical segments) N_{st} per cluster.

The distance between the clusters R_{cl} should be taken as R_w

$$R_{cl} = 18 \left(\frac{2V_{cl}}{F} \right)^{-1/3}, \quad (26a)$$

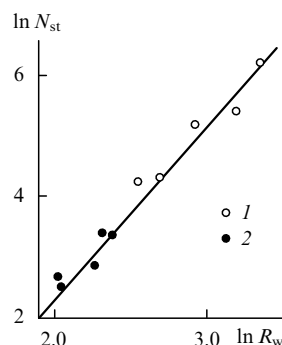


Figure 5. Number of statistical segments N_{st} in a cluster vs. its radius R_w for amorphous (1) and amorphous-crystalline (2) polymers under the assumption that the sizes of fractal and percolation clusters are equal.

where V_{cl} is the density of the cluster network and F is the cluster functionality.

Figure 5 presents the dependence of N_{st} on R_w for five amorphous vitreous and five amorphous-crystalline polymers.⁸ It can be seen that this correlation is fully consistent with relation (26). The d_f value of the cluster structure determined from the slope of the straight line is ~ 2.75 . The fractal dimension of the cluster in the WS model lies in the range of 2.25 – 2.75 ,⁸⁸ which is in agreement with the above estimate.

The fractal dimension for the structure of the amorphous polymer can be found from the relation⁹⁴

$$d_f = (d - 1)(1 + \mu), \quad (27)$$

where μ is the Poisson coefficient.

For a cluster structure with $d_f \approx 2.75$, the μ value is equal to ~ 0.375 , which is consistent with the known μ values for amorphous vitreous polymers.^{95,96}

As an example of fractality displayed in polymers at a macroscopic level (a secondary structural element), we shall consider the growth of a crack in a film of amorphous vitreous polyarylate-sulfone.⁹⁷ The surfaces of cracks have irregularities of at least two scales: ~ 20 μm (Fig. 6a) and ~ 20 mm (Fig. 6b). This provides grounds for describing them in terms of fractal models.^{98–100} The triangular profile throughout the whole period of growth of the crack allows the use of the relationship proposed by Mosolov⁹⁸

$$d_{sk} \propto r_{sk}^{D_{sk}/2}, \quad (28)$$

where d_{sk} is the crack opening, r_{sk} is the distance from the crack top and D_{sk} is the fractal dimension of the crack.

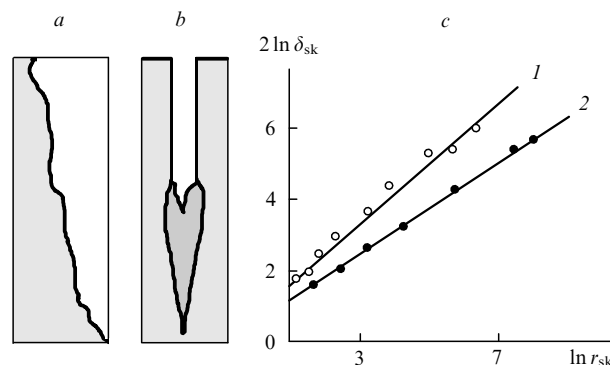


Figure 6. Crack coast-line (a), general view of a stable crack (b) and opening of the crack δ_{sk} vs. the distance to its top r_{sk} (c) for polycarbonate (1) and polyarylate (2).⁸

Figure 6c shows the plots for the variation of δ_{sk} vs. r_{sk} for two amorphous polymers; the plots correspond to relation (28). In other words, a stable crack in polymer film samples is a stochastic fractal with the dimension $D_{sk} \approx 1.48$. The linearity of plots shown in Fig. 6c reflects the self-similarity of the crack at different stages of its growth. Thus, polymers also exhibit fractal properties at the macroscopic level.

The examples considered above do not reflect the whole diversity of manifestation of fractality in polymers. Nevertheless, they help to understand the meaning of the term ‘multifractality’ as applied to polymers.

III. Fractal characteristics of macromolecules

Condensed systems start to behave as polymers after a certain molecular mass has been attained and a network of macromolecular entanglements or chemical nodes has been formed.⁵⁶ In consideration of condensed polymers, it is especially important to describe the sections of the macromolecule between the points of chemical cross-linking or entanglements.⁵⁵ The deformability and mobility of these sections largely determine the macroscopic properties of polymers.^{56, 101} The general physical grounds which account for the fractality of these chain sections are considered below in relation to epoxy polymers.

To determine the fractality of an object, three aspects are usually considered.¹² First, as noted above, a real physical object possesses fractal properties only in a definite scale range (see Fig. 1). The boundary sizes for a macromolecular section can be determined using the data of several publications.^{22, 35, 102} The lower boundary is related to the finite size of a structural element; in terms of the cluster model, this is the length of the statistical segment l_{st}

$$l_{st} = l_0 C_\infty, \quad (29)$$

where l_0 is the length of a chemical bond and C_∞ is the characteristic ratio.

For most polymers, $l_0 = 0.125$ nm (see Ref. 90), the minimum $C_\infty = 2$ (see Ref. 91); therefore, the minimum possible l_{st} is 0.25 nm. This value is in good agreement with the experimental estimate of the lower limit of fractality in polymers (~ 0.3 nm²²) and should be accepted as the L_{min} for the chain section between chemical cross-links. The length of this section L_s can be taken as the upper limit. For most of the epoxy polymers considered, this value is in the range from ~ 1.6 to 7.4 nm, which is also consistent with the data of Refs 22 and 35.

The second aspect is associated with the self-similarity of the object considered. A section of the macromolecule between chemical cross-linking points represented by a freely jointed Kuhn chain or by a chain with free or hindered rotation about the bond⁹¹ is simulated by a broken line having the topological dimension $d_t = 1$.³ In the case of simulation by the freely jointed Kuhn chain, the broken line consists of N_s statistical segments of length A , each of them being simulated by a straight-line segment. These straight-line segments are standard self-similar objects but the chain sections consisting of them are self-similar only when their lengths L_s and the A values vary proportionally. For the epoxy polymers in question, this condition is fulfilled;¹⁰³ therefore, these sections are self-similar objects.¹⁰⁴

Finally, the third aspect concerns determination of the fractal dimension D of an object.¹² For fractals, the condition

$$D > d_t.$$

should hold.¹⁶ In the case where a macromolecular section between chemical cross-linking points is represented by the freely jointed Kuhn chain, the following equality should hold:¹⁰¹

$$R_s^2 = L_s A, \quad (30)$$

where R_s is the smallest (straight-line) distance between chemical cross-links.

A fractal broken line can be described by the relation⁸⁸

$$\frac{L}{a} = \left(\frac{R}{a}\right)^D, \quad (31)$$

where L is the length of the line, R is the straight-line distance between its ends, a is the scale of measurements in the macromolecule.

By dividing both parts of Eqn (30) by A^2 , we find that

$$\frac{L_s}{A} = \left(\frac{R_s}{a}\right)^2, \quad (32)$$

i.e., a freely jointed Kuhn chain is a broken line with dimension 2 provided that condition (30) is fulfilled. Note that in this case, the chain is a fractal because $D > d_t$. Since the random-walk dimension d_w for this model of a macromolecule is also equal to 2,⁶⁶ the spectral dimension d_s of the chain can be estimated [see Eqn (8)]. For a freely jointed Kuhn chain, it is also equal to 2.

Let us consider conditions under which $d_s = 2$. For a real polymer, with allowance for the effect of excluded volume, one can write that⁵⁶

$$D = \frac{2d_s}{\alpha - d_s}, \quad (33)$$

where

$$\alpha = d_s + \frac{2(d_s + 2)}{d + 2}. \quad (34)$$

When $D = d_s = 2$, Eqns (32) and (34) are correct only when $d = 2$. This means that the ranges of variation of the fractal dimension of a macromolecule section between cross-linking points are $d_t < D \leq d$ or $1 < D \leq 2$.

However, the freely jointed Kuhn chain is the most idealised model for a real macromolecule; therefore, there exist several corrections taking into account specific features of the polymer structure. Thus, for chains in which $L_s/A < 10$, condition (30) no longer holds. The modified condition is written as follows⁹¹

$$R_s^2 = L_s A - \frac{A(1 - e^{-2L_s A})}{2}. \quad (35)$$

Equation (35) points to a decrease in L_s at a constant R_s and, hence, to a decrease in D , in conformity with Eqn (31). Note that the condition $L_s/A < 10$ holds for nine of the ten specimens of epoxy polymers; this automatically means that $D < 2$.⁸

The hindrance of rotation of the macro-chain around bonds, which necessarily occurs in a vitreous polymer, accounts for the decrease in the real A value to A_{rot} according to the relation⁹¹

$$\sigma^2 = \frac{A}{A_{rot}}, \quad (36)$$

The hindrance parameter σ can be determined from the empirical equation¹⁰⁵

$$T_g = C(\sigma - 1), \quad (37)$$

where T_g is the experimental glass transition temperature and C is a constant (for carbon-chain polymers, $C = 270$ K).

Now we can calculate non-fractal values R_s and L_s as functions of the cross-linking density v_s using Eqn (29) and the relation¹⁰⁴

$$L_s = \frac{F_{ch}}{2Sv_s}, \quad (38)$$

where F_{ch} is the functionality of a chemical cross-linking point (hereinafter, we assume that $F_{ch} = 4$) and S is the cross-section area of the macromolecule.

The results of calculation of D as a function of v_s for the epoxy polymers considered here using Eqn (31) with $a = A_{rot}$, $L = L_s$ and $R = R_s$ are shown in Fig. 7, curve 1. It can be seen that the allowance for the hindered character of rotation has resulted in a monotonic decrease in D following an increase in v_s . As has been shown,¹⁰¹ this implies a decrease in the mobility (deformability) of

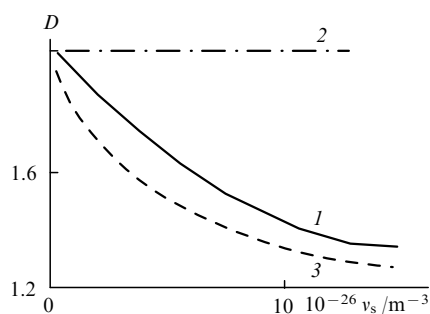


Figure 7. Fractal dimension D of a macromolecule section between chemical cross-linking points vs. cross-linking density v_s for epoxy polymers based on epoxy oligomers and amino-containing curing agents. The D values were found from Eqn (31) for $a = A_{\text{rot}}$ (1), A (2) and 0.25 nm (3).

the macromolecule section between the points of chemical cross-linking.

The calculation of D from Eqn (31) but for $a = A$ gives $D \approx 2$ irrespective of v_s (Fig. 7, curve 2). Finally, when persistence of the chain section is taken into account, *i.e.* the chain parameters vary according to Eqn (35), a somewhat higher D value is obtained, although the difference does not exceed $\sim 3\%$. The change in the scale of measurements also changes the fractal dimension of the chain. Curve 3 in Fig. 7 reflects the dependence of D on v_s for $a = 0.25 \text{ nm}$ (*i.e.*, for the minimum size). This curve runs parallel to curve 1 but is characterised by somewhat lower D (by $\sim 3\% - 13\%$). Our choice of the scale of measurement of A_{rot} (or l_{st}) is due to the fact that it reflects the real state of the chain under particular conditions ('natural' scale of measurements).

Let us discuss in more detail the physical meaning of the fractal dimension D of a chain section between chemical cross-linking points (or between entanglement points). Substitution $L = L_s$, $R = R_s$ and $a = l_{\text{st}}$ in Eqn (31) gives the relation^{101, 106}

$$\frac{L_s}{l_{\text{st}}} = \left(\frac{R_s}{l_{\text{st}}} \right)^D, \quad (39)$$

which implies that when $D = 1$, $L_s = R_s$, *i.e.* the chain between the cross-links is completely stretched and loses the capacity for deformation (mobility). This is consistent with the data of a publication,⁵¹ according to which $D = 1$ corresponds to a completely uncoiled chain (see Table 2). Recall that the condition $D = 1$ means that the given section of the macromolecule has completely lost fractal properties. When $D = 2$, we obtain the maximum possible length of the chain section L_s for a fixed R_s and the greatest l_{st} , *i.e.* the chain deformability (mobility) is the most pronounced in this case. Note that the highest stretching ratio λ_{max} for a given chain section is equal to L_s/R_s .^{107, 108} It is clear that $D = 2$ is attained for rubbers, and intermediate values, $1 < D < 2$, describe different degrees of mobility of a macromolecule section between chemical cross-links (entanglements). This quantitative measure of mobility is convenient because the fractional part of D provides actually a relative measure of mobility, irrespective of the structure of the macromolecule or other features of the polymers.⁸²

Let us consider the physical reasons for the fractality of the macromolecule, *i.e.* for the dependence of the chain length L_s on the scale of measurement A_{rot} or l_{st} . The first reason is that L_s can change upon conformational changes in the macromolecule due to variation of C_∞ , *i.e.* the bond angle θ_v can change according to the equation⁹¹

$$\sigma^2 = C_\infty \frac{1 - \cos \theta_v}{\cos \theta_v}. \quad (40)$$

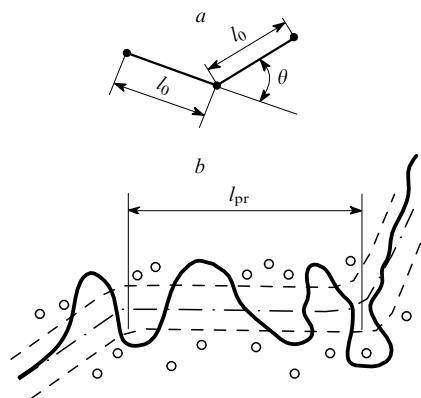


Figure 8. Schemes of two adjacent bonds of a macromolecule (a) and the enveloping tube (b).

Figure 8a shows schematically two consecutive bonds with the length l_0 . The total length of such a section l projected onto the axis of one of the bonds is equal to

$$l = l_0 + l_0 \cos \theta_v. \quad (41)$$

It is clear that the smaller θ_v , the greater the second term in Eqn (41) and the greater L_s . The maximum L_s value is attained for tetrahedral angles ($\theta_v = 70.5^\circ$).⁹¹ The distance between the cross-links determined in this way (we shall call it conformational length L_{conf}) is obviously equal to

$$L_{\text{conf}} = \frac{L_s l}{2l_0}. \quad (42)$$

Another physical representation of the effect in question is the use of the reptation model,⁴¹ in which a macromolecule is assumed to be encapsulated in a 'tube' of a finite thickness (Fig. 8b). In this case, the topological skeleton of the chain consists of N_{pr} units of length l_{pr} , which form a primitive path with the length

$$L_{\text{pr}} = N_{\text{pr}} l_{\text{pr}}.$$

It is also assumed that the ends of fragments of the primitive path with the length l_{pr} are fixed in a definite manner; therefore, the N_{pr} and L_{pr} values can be found fairly easily using l_{pr} . The L_{pr} value can be expressed as follows:⁴¹

$$L_{\text{pr}} = L_s \frac{A_{\text{rot}}}{l_{\text{pr}}}, \quad (43)$$

where l_{pr} is assumed to be equal to the distance between clusters R_{cl} , which can be calculated from Eqn (26a).

The length of the fractal broken line L_f is expressed in the following way:³

$$L_f = L' a^{1-D}, \quad (44)$$

where $L' > 1$ is the length of the non-fractal line.

Since the L_s value determined using Eqn (38) is calculated, in the first approximation, as the length of a cylinder with the cross-section area S , *i.e.* of a non-fractal object, it can be assumed that $L' \approx L_s$. If the two above examples point to the presence of fractal properties of a section between chemical cross-links (entanglements), the following relation should be obeyed:

$$L_f \approx L_{\text{conf}} \approx L_{\text{pr}}. \quad (45)$$

Relation (45) actually holds (with a deviation of $\pm 20\%$) for epoxy polymers based on bisphenol A and cured by diamine (EP-1) or anhydride (EP-2) (Fig. 9).⁴⁷ This indicates that the fractality of the macromolecule section between chemical cross-linking points (entanglements) in a vitreous polymer is due to known mechanisms of the change in the statistical rigidity.

It follows from Eqn (39) that the loss of fractality by a chain section, irrespective of the scale of measurements, takes place in the case of full stretching of this section between cross-linking

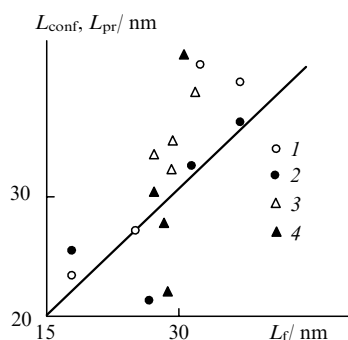


Figure 9. Relationships between the conformational length L_{conf} (1, 3) and primitive path L_{pr} (2, 4) of the chain section between chemical cross-linking points and its fractal length L_f for EP-1 (1, 2) and EP-2 (3, 4).

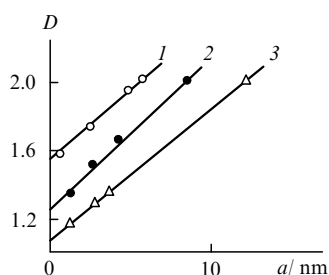


Figure 10. Fractal dimension of the macromolecule section between chemical cross-linking point (D) vs. scale of measurement a for EP-1. $v_s \times 10^{-27} / \text{m}^{-3}$: (1) 0.2, (2) 0.6, (3) 1.7.

points (entanglements), *i.e.* when $L_s = R_s$. In addition, for $a \rightarrow 0$, the $L(a)$ value would tend to a final limit equal to the length of the straight line. Figure 10 shows the $D(a)$ plots for EP-1. It can be seen that, when $a \rightarrow 0$, the fractality of the chain section between cross-linking points is retained. Therefore, the behaviour of this section of a macromolecule is more intricate than that of a mere fractal broken line; this can be due to a more complex structure of the macromolecule. Indeed, transition to a non-fractal behaviour requires not only that condition $L_s = R_s$ be fulfilled, as for an ordinary broken line, for example, for a coast-line, but also that a conformation condition — Eqn (30) — be fulfilled. In this case, it is necessary that the bond angle θ_v reach a value which complies with the equality (for $l_{\text{st}} = A$)

$$C_\infty = \frac{A}{l_0} \cos \frac{\theta_v}{2}. \quad (46)$$

A chain for which $D \neq 1$ can be referred to as ‘true fractal’.

Examination of Eqns (26a) and (38) leads to yet another, at least formal, reason for the fractal properties of the section of a macromolecule between the cross-links. For a given cross-linking density, the L_s value (unlike R_s) depends on the cross-sectional area S of the macromolecule, which should also result in the variation of D . Figure 11 shows the dependences of D on S for two arbitrary v_s values, namely, 1×10^{27} and $2 \times 10^{27} \text{ m}^{-3}$. It can be seen that D rapidly decreases as S increases; when $S \approx 0.80$ and 0.55 nm^2 , respectively, D reaches the lower limit ($D = 1$). This implies full ‘freezing’ of the molecular mobility of the chain,¹⁰¹ which should result in a high fragility of the polymer. This assumption is confirmed in practice. It is known that polystyrene and poly(methyl methacrylate) are fragile polymers ($S = 0.698$ and 0.638 nm^2 , respectively) and poly(n-dodecyl methacrylate) and poly(n-octyl methacrylate) are highly fragile polymers ($S = 1.766$ and 1.351 nm^2 , respectively).¹⁰⁹

Thus, the section of the macromolecule between chemical cross-links and physical entanglements possesses fractal properties. This is due to the fact that the length of this section is shorter than the size of the macromolecule. This factor is due to various

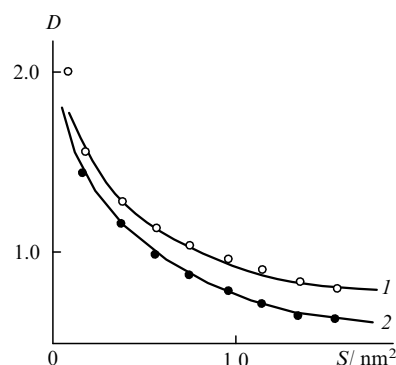


Figure 11. Fractal dimension of a section of macromolecule between chemical cross-linking points (D) vs. cross-sectional area of the macromolecule S . $v_s \times 10^{-27} / \text{m}^{-3}$: (1) 1, (2) 2.

steric restrictions, which induce deviations from the behavior predicted by Eqn (30). In the general case, Eqn (30) is valid for a non-perturbed (quasi-equilibrium) coil;³² therefore, the fractality of the chain section considered can be interpreted as being due to the deviation from the quasi-equilibrium state.¹² The deviation changes the degree of the ‘sinuosity’ of the macromolecular section (*i.e.* the length of the statistical segment); therefore, the l_{st} (or A , or A_{rot}) value can be considered to be a ‘natural’ scale of measurement. Since the structure of a macromolecule is more complex than the geometric image represented by a broken line, its behaviour would also be more complicated; this is confirmed by the change in D when $a \rightarrow 0$. In other words, the section of a macromolecule between cross-links has configurational fractal properties, stipulated by the mutual arrangement of the rigidity sections of the macromolecule, and conformational fractal properties, caused by the state of the bonds within this rigidity section (statistical segment).

1. The dimension of the sections of a macromolecule between topological fixing points

A cross-linked polymer is formally one giant macromolecule (fractal cluster); therefore, the models considered above provide the dimension d_f of exactly this cluster. The Vilgis concept^{60,61} assumes the existence of several clusters of this type and linear macromolecules between them. In practice, parameters used more widely are the density of the network of nodes (chemical cross-links) v_s or the molecular mass of the macromolecular section between the cross-links M_s , which are related to each other in the following way:

$$v_s = \frac{\rho N_A}{M_s}, \quad (46a)$$

where N_A is the Avogadro number and ρ is the polymer density.

In a study by Sandakov *et al.*,⁴⁹ the term ‘molecule’ for cross-linked polymers was used to denote only a section of the macromolecule with the molecular mass M_s , because it is known⁴³ that it is the parameters v_s and M_s that determine the properties of network polymers. In addition, the difference between the scales of fractality of a big macromolecular cluster and the polymer structure in the vitreous state should be taken into account, *i.e.* one should have in view lengths of the order of ~ 0.3 – 5.0 nm where a macromolecule is a fractal.²²

Below we consider practical aspects of the estimation of the fractal dimension D of a macromolecule section between chemical cross-linking points with allowance for these statements as well as for those considered in the preceding Sections. This approach differs fundamentally from that of the Cates⁵⁵ and Vilgis models.^{60,61} All the foregoing is valid not only for a network of chemical bonds but also for a network of macromolecular entanglements in linear polymers.

Several methods for the estimation of the D value exist. One method makes use of the relation¹¹⁰

$$D = \frac{\ln n_{st}}{\ln l_{st}}, \quad (47)$$

where n_{st} is the number of statistical segments of length l_{st} in a chain fragment between entanglements (chemical cross-links).

Yet another variant of calculation of D is given by Eqn (39). The following relation has been obtained:¹¹¹

$$\frac{2}{\varphi_{cl}} = C_{\infty}^D, \quad (48)$$

where φ_{cl} is the relative part of local order (clusters) in the polymer.

The relationship between D and d_f [see Eqn (27)] is reflected by the expression:^{112, 113}

$$D = \frac{\ln n_{st}}{\ln(4 - d_f) - \ln(3 - d_f)}. \quad (49)$$

The D values estimated using Eqns (39) and (47)–(49) vary from 1 to 2.

The use of fractal analysis makes it possible to relate molecular parameters to characteristics of supermolecular structure of polymers. Figure 12 illustrates the linear correlation between D and d_f [d_f was estimated from Eqn (27)] for epoxy polymers. When the molecular mobility is suppressed ($D = 1$), the structure of the polymer has the fractal dimension $d_f = 2.5$, which corresponds to $\mu = 0.25$. The given value of the Poisson coefficient corresponds to the boundary of ideally brittle structure; at $\mu < 0.25$, the polymer is collapsed without viscoelastic or plastic dissipation of energy.³ This is fully consistent with the Kausch conclusion¹¹⁴ stating that any increase in the molecular mobility enhances dissipation of the mechanical energy supplied from the outside and, as a consequence, increases plasticity of the polymer. When $D = 2$ the d_f value is equal to 3, which corresponds to $\mu = 0.5$, typical of the rubbery state.

Figure 12b shows the variation of D vs. v_s for the epoxy polymers considered here. The dependence is non-linear, the D value decreases with an increase in v_s ; even for small v_s values, a substantial decay in D is observed. It is of interest that the end of this decay and transition to a much slower decrease in D takes place at $v_s \approx 8 \times 10^{26} \text{ m}^{-3}$, which corresponds to ~ 10 monomer units between the cross-links. Actually, this can be interpreted as transition to densely cross-linked epoxy polymers in which an increase in v_s influences the suppression of the molecular mobility to a substantially lower degree than in the region where $v_s = 0.8 \times 10^{27} \text{ m}^{-3}$ (see Ref. 8).

If the conformational and/or physical state of the section between cross-links are assumed to coincide with that of the whole

macromolecule (see Table 2), the plot shown in Fig. 12b allows one to judge the nature and the ranges of variation of these states. The first characteristic dimension $D = 2$ corresponds to the state of a statistical coil in an ideal solvent, the second one $D \approx 1.67$ corresponds to an impermeable coil in a good solvent, the third one $D = 1.50$ is matched by a permeable coil (the state typical of rigid-chain polymers), and the fourth value, $D = 1$, describes a completely uncoiled macromolecule.⁵⁰ It can be assumed that the increase in the cross-linking density between the above D values is accompanied by gradual transition from a state with greater D to a state with smaller D . Thus, depending on v_s , a network polymer can be both a rubber and a rigid-chain polymer.¹¹⁵ Therefore, it is evident that the knowledge of these regularities is important for controlling the properties of network polymers.

Now we attempt to estimate D within the framework of the theoretical views on polymer fractals.^{22, 35, 55, 60–63} It is assumed⁶⁶ that the fractal dimensions d_s , d_w and D are related to one another via an expression similar to Eqn (8). The relationship between the parameters d_s and D has been considered.⁶⁵ It is believed that d_s is a dynamic value which responds to a change in the conditions of the interaction of a macromolecule with its surrounding and D is a static parameter. However, in our opinion, the opposite situation occurs in reality; this is indicated by the following facts, some of which have been noted above. It has been shown experimentally⁶⁹ that a twofold increase in the cross-linking density does not change d_s , while, according to the plot shown in Fig. 12b, v_s has an appreciable influence on D . Moreover, the monomer and the cross-linked epoxy polymer have nearly identical d_s values (see Table 4). Helman *et al.*⁶⁶ proposed a fractal model in which they employ the notion of weightless bridges. In accordance with this model, d_s is equal to D when the concentration of these bridges is relatively high. However, theoretical analysis and computer simulation^{10, 67} show that the inclusion into consideration of bridges of a finite length does not change the spectral dimension of the system. With allowance for this fact, it was assumed that the d_s value would be equal to that determined experimentally for an epoxy polymer in a three-dimensional space, $d_s = 1.44$ (see Ref. 69).

Two hypotheses can be used to estimate d_w — the Alexander – Orbach (AO) and Aharoni – Stauffer (AS) hypotheses.¹⁰ The AO hypothesis is based on the following relation:

$$d_w = \frac{3}{2} d_f,$$

while the AS hypothesis assumes the relation

$$d_w = 1 + d_f.$$

It is considered that d_w is determined by the properties of the supermolecular structure of epoxy polymers, namely, by the degree of local order in them. This assumption arises due to the well-known succession of relationships between the diffusion process and d_w ,²⁸ between the diffusion process and the fluctuation free volume f_{iv} ,¹¹⁶ and between f_{iv} and the cluster structure.¹¹⁷ Therefore, the fractal dimension of the cluster structure of cross-linked polymers,^{102, 107} estimated from Eqn (27), is taken to be d_f . Since the D value is determined for an Euclidean space with $d = 2$, it was also assumed in Eqn (27) that $d = 2$. The d_s value was found for a three-dimensional space; therefore, a graph¹¹⁸ for converting d_s from three- to two-dimensional space was used in subsequent calculations. The D values were further calculated from Eqn (8) in terms of the AO and AS hypotheses. Figure 13 shows the dependences of D on v_s calculated from Eqns (8) and (39). The dependences of D on v_s and the absolute magnitudes of D are in good agreement, especially when the AO hypothesis is used. When v_s is low, the D values calculated from Eqn (39) deviate towards the curve estimated using the AO hypothesis. Nevertheless, the discrepancy between the calculations by two methods does not exceed 10%.

Thus, the fractal dimension of a section of the macromolecule between chemical cross-linking points in network polymers varies

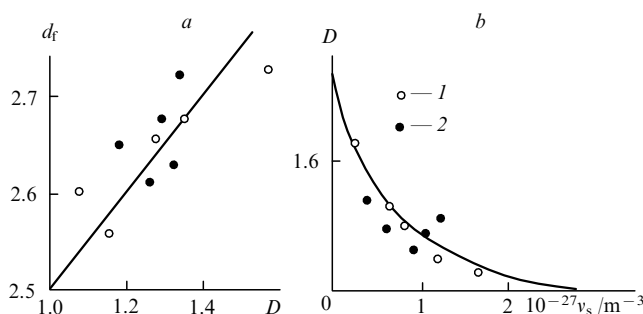


Figure 12. Correlation between fractal dimensions of the structure d_f and the chain section between chemical cross-linking points D (a) and the $D(v_s)$ dependence (b) for EP-1 (1) and EP-2 (2).¹⁰⁶ The straight line was drawn through the points: $D = 1.0$, $d_f = 2.5$ and $D = 2.0$, $d_f = 3.0$.

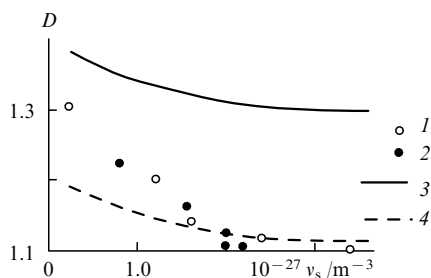


Figure 13. Fractal dimension of the chain section between chemical cross-linking points D vs. cross-linking density ν_s . Calculation using Eqn (39) for EP-1 (1) and EP-2 (2); calculation using Eqn (8) for EP-1 and EP-2 in terms of the AS (3) and AO (4) hypotheses.

over limits close to those predicted for a fractal broken line, *i.e.* $1 \leq D \leq 2$. The dimension D can serve as a measure of the molecular mobility and is related to the fractal dimension of the cluster structure of epoxy polymers d_f . The dependence of D on d_f can also be derived theoretically. The calculation procedures proposed take into account the influence on D of characteristics of the molecular and topological structural levels of cross-linked polymers.

2. The concept of macromolecular skeletons

a. The model of a network polymer

The model of network polymers considered below describes quantitatively the formation of structure (and, hence, properties) and is based on fundamental principles of physics. The initial parameters used for cross-linked systems are the ν_s value (topological characteristics) and some generally accepted molecular parameters. Since the chemical cross-linking processes are complex, the model makes use of the simplest scheme of structure formation, which does not take into account, for example, the decrease in the rate of structure formation with time when one structure element starts to influence the conditions of formation of an adjacent element. An example of taking account of effects of this type has been reported.¹¹⁸ Although this scheme is simple, it provides a quantitative description of the processes considered and the structures formed.

One point of the model under discussion is estimation of the relationship between ν_s and the level of local order in the structure of epoxy polymers, which is characterised by the density V_{cl} of the cluster network of macromolecular entanglements.^{101–103} A parameter characterising the level of local order more rigorously is the fraction of clusters φ_{cl} in the polymer.

Curing is supposed to be a turbulent process because it requires mobility of structural elements and takes place in a viscous medium. In addition, transition to a turbulent mode implies an increase in the degree of ordering, *i.e.* self-organisation of dissipative structures such as clusters.¹¹⁹ A fundamental property of turbulent flows is fractality of turbulent structures.^{3, 10} It is generally believed that dissipation of energy in three-dimensional turbulent flows is concentrated on a set with a non-integral fractal dimension. However, experimental data on the beginning of fluctuations indicate that the small-scale properties of a turbulent flow cannot be described by virtue of fractals.³ Therefore, turbulent dissipative structures are described using 'non-homogeneous fractals,' the rules of formation of which are chosen at random at each step of scale hierarchy in accordance with some probability distribution.^{120, 121} In this case, the transfer of energy is described by virtue of random fragmentation model with the assumption that no correlations exist between stages of the process. Nevertheless, it is possible to calculate the fractal dimension of turbulent structures (D_f), which is defined by the relation

$$\langle N_n \rangle \sim L_n^{-D_f}, \quad (50)$$

where N_n is the number of active vortices at an n -th fragmentation step, L_n is the scale of the n -th vortex, and D is estimated using the following equation:¹⁰

$$D_f = 3 + \log_2 \beta, \quad (51)$$

in which β is the fraction of the volume occupied by vortices of the scale L_n .

As a first approximation, it can be assumed that $D_f = d_f^t$, where d_f^t is the fractal dimension of the topological structure of the polymer, which can be found from Eqn (27).

It is clear that the chain fragments with the molecular mass M_s are considered in a plane ($d = 2$) and the formation of clusters is discussed in a volume ($d = 3$). The D value calculated from Eqn (39) for a two-dimensional fractal can be used to find the value for a three-dimensional fractal by applying Eqn (27) to the dimension d_f^t . This method is not highly accurate but simple. Equation (51) makes it possible to determine the fraction of volume β occupied by vortices of the L_n scale. Assuming that the β and φ_{cl} values are equal, the V_{cl} value can be calculated from the relation

$$V_{cl} = \frac{\varphi_{cl}}{S l_0 C_\infty}.$$

Comparison of the V_{cl} values found in this way with those obtained experimentally⁴⁷ for systems EP-1 and EP-2 showed that the two methods provide the same order of magnitude. Nevertheless, to attain better agreement between the results, it can be assumed that not all the active turbulent vortices are converted into local order regions; in general, this is obvious due to the fluctuational nature of these regions.⁸⁹ This means that $\varphi_{cl} = C\beta$, where C is a proportionality coefficient. Assuming that for EP-1 and EP-2, $C = 0.6$, we obtain a much better quantitative agreement between experimental and calculated data. It is clear that the coefficient C reflects the influence of variable characteristics of curing such as temperature, time, viscosity of the medium, *etc.* The fact that the dimension of non-homogeneous fractal D_f is always greater than the dimension of the corresponding homogeneous fractal d_f^t might serve as yet another reason for the inconsistency between the φ_{cl} and β values, mentioned above.¹²² The condition $D_f > d_f^t$ implies a decrease in β in the calculations using Eqn (51).

Fractality of the structures of polymers influences their properties. According to modern concepts,^{123–125} the glass transition of amorphous polymers is regarded as the formation of 'frozen' local order (dissipative structures). Generally, for amorphous systems, this is considered to be a complex and hierarchically multistage process. The first stage involves the formation of seeds of microcrystals, which are unable to grow and serve as a sort of substrate for deposition of amorphous clusters. The second stage is characterised by self-organisation of mesoclusters.¹²⁶ As applied to the glass transition of polymers, these processes can be specified in the following way. The first stage starts at the temperature of so-called liquid–liquid transition T_{ll} , in which regions of dynamic short-lived local order are formed.²³ At the glass transition temperature, avalanche-like accumulation of clusters takes place, which characterises the formation of 'frozen' local order (the second stage). For this process,

$$\tau^* \propto (R^*)^{d_f}, \quad (51a)$$

where τ^* is the time before the onset of this process and R^* is the critical cluster size.⁹⁸

Since the temperature–time superposition is correct for polymers, we assume that $R^* \propto l_{st}$ and write relation (51a) in the following form

$$T_g \propto l_{st}^{-\alpha}.$$

The dependence of the experimental T_g values¹¹² on l_{st} for epoxy polymers can be represented by a correlation function. In addition, $\alpha \simeq 0.28$, which complies with the necessary condition

$\alpha = d - d_f$.⁸⁸ Hence, the change in T_g upon the variation of v_s is also an indication of the fractal structure of network polymers.

Note that the behaviour of network polymers is in agreement with several other fundamental physical principles. Let us illustrate this by two examples. An integral stoichiometry implies stability and ordering of the structure of a compound.³ This is confirmed by the data of Beloshenko *et al.*,¹⁰² according to which the maximum degree of local ordering in epoxy polymers is attained when an oligomer and a curing agent are taken in stoichiometric amounts, *i.e.* when $K = 1.0$ (or is close to 1).

Structure parameters and characteristics of properties of epoxy polymers are not random values either. Thus the length of statistical segment l_{st} obeys the automodelling relation

$$\frac{l_{sti}}{l_{st(i+1)}} = \Delta^{1/m}, \quad (52)$$

where $\Delta = 10$ and m varies according to a geometric progression law

$$m = 2, 4, 8, 16, 32, \dots, 2^n, \dots, \infty. \quad (53)$$

Hence, formation of the structure and properties of epoxy polymers during curing is determined by fundamental physical principles. This is accompanied by the change in the characteristic ratio C_∞ (molecular characteristics), although the structure of the macromolecule remains invariant. The use of the above physical principles even in the simplest version provides a correct description of the structure and properties of network polymers.

b. Scaling representation of a macromolecule

A number of methods exist for the modelling of polymers at a molecular level. One of the most widely used methods is scaling presentation,⁵² according to which the diameter ϕ of the 'tube' in which the macromolecule is enclosed (it is equal to the distance between the entanglement points) can be estimated from the ratio⁷²

$$\phi^2 = C_\infty \frac{M_s l_0^2}{m_0}. \quad (54)$$

The main difference between physical entanglements (loops) and chemical cross-links is that the former allow creeping of chains. The density of both types of link are determined using the same rubber elasticity equation, a factor of 0.8 being frequently added to take creeping into account.⁷²

Yet another representation of a macromolecular chain as a fractal is considered below. Olemskoy and Flat¹²⁷ have noted that the concept of fractals rather than description of an observed geometric image is usually applied to condensed media. As regards a macromolecule, modelled by a freely jointed chain consisting of statistical segments, one can hardly find a geometrical image more vivid than a fractal broken line. In addition, it should be noted that representation of a macromolecule by either one-dimensional (as a curve) or three-dimensional (as a cylinder) object appears to be a fairly rough approximation in view of the real structure of a macromolecule, *i.e.* the presence of side chains, flexible bonds, rigid segments, *etc.*

As noted above, a change in the density of chemical cross-linking v_s in epoxy polymers results in an extremal variation of the characteristic ratio C_∞ with the minimum $K \simeq 1.0$.¹¹⁵ If the section of a macromolecule between chemical cross-links is modelled by a freely jointed chain, the use of known L_s and l_{st} values results in a typical fractal dependence¹¹⁹

$$N_{st}(\xi l_{st}) = \xi^{-D} N_{st}(l_{st}), \quad \xi < 1, \quad (55)$$

where N_{st} is the number of statistical segments per fragment of a macromolecule with the molecular mass M_s , and ξ is a similarity parameter.

With the assumption that $L_s = \text{const}$ and $K = 1.0$, $\xi = 0.85$ was obtained; with $L_s = \text{const}$ and $K > 1.0$, the calculations gave $\xi = (0.85)^{1/2} = 0.926$. The calculation of the dimension D from

Table 6. Calculated molecular characteristics of epoxy polymers.⁸

Polymer	K	D	C_∞		
			I	II	III
EP-1	0.50	2.06	5.23	4.83	5.28
	0.75	1.60	4.32	6.97	3.50
	1.00	1.25	3.38	9.94	3.68
	1.25	1.35	3.75	8.89	3.19
	1.50	1.50	4.05	7.68	3.34
EP-2	0.50	1.85	5.27	6.54	5.35
	0.75	1.43	3.98	8.89	4.69
	1.00	1.32	3.40	9.24	3.37
	1.25	1.35	3.70	9.24	3.90
	1.50	1.55	4.10	7.96	4.29

Note. The following designations are used: I — data of Ref. 121, II — calculation by Eqn (54), III — calculation by Eqn (57).

Eqn (55) gave 1.17. Thus, when the condition mentioned above is fulfilled, the section of a macromolecule between chemical cross-linking points can be represented as a fractal. Variation of K changes the cross-linking density v_s and, hence, L_s . As a consequence, the chain ceases to be a self-similar fractal. Nevertheless, it still can be modelled by a non-homogeneous fractal with the same fragmentation step but with a variable D value, determined from relation (39). The D values calculated in this way are listed in Table 6.

The results of calculation of the characteristic ratio C_∞ from Eqn (54) are inconsistent in kind with the data obtained by Jean *et al.*¹²⁸ Indeed, the maximum rather than the minimum C_∞ is attained at $K = 1.0$. Since

$$\phi^2 \propto v_s^{-2/3}, \quad M_s \propto v_s^{-1},$$

then, according to Eqn (54), the C_∞ value should be proportional to $v_s^{1/2}$. In other words, an increase in the density of cross-links should increase the chain flexibility, which is inconsistent with the extremal increase in the glass transition temperature of epoxy polymers.^{115, 129}

Let us consider the reasons for this inconsistency.

Since

$$C_\infty l_0 = l_{st}, \quad \frac{M l_0}{m} = L_0,$$

multiplication and division of Eqn (54) by l_{st}^2 gives the relation⁸

$$\frac{L_0}{l_{st}} = \left(\frac{R_s}{l_{st}} \right)^2, \quad (56)$$

which is similar to Eqn (39). Comparison of Eqns (39) and (56) shows that the scaling relation (54) is a specific case of the fractal formula (39) for $D = 2$. For the epoxy polymers considered, condition $D = 2$ does not hold (see Table 6); this may account for the discrepancy found. Using relations (39) and (56), the scaling equation (54) can be written in a more general form

$$a^D = C_\infty^{D-1} \frac{M_s l_0^D}{m}. \quad (57)$$

The calculation of C_∞ using Eqn (57) give values that are in good agreement with the results obtained by Jean *et al.*¹²⁸

It has been shown⁹⁰ that in the case of linear polymers, the following empirical correlation is obeyed for physical entanglements

$$R_s \simeq 10 C_\infty. \quad (58)$$

Taking into account the data presented above, the same (or similar) correlation should be expected for chemical cross-links in network polymers.

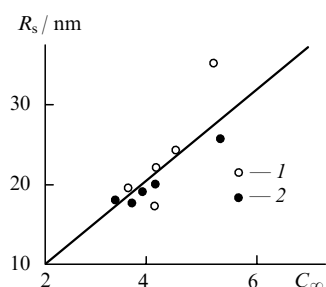


Figure 14. Distance between chemical cross-linking points R_s vs. characteristic ratio C_∞ for EP-1 (1) and EP-2 (2).⁸

The relationship between the C_∞ values found using Eqn (57) and R_s calculated using Eqn (26a) is linear

$$R_s \approx 5C_\infty, \quad (59)$$

which is illustrated by Fig. 14.

Equations (58) and (59) are qualitatively similar and the discrepancy of numerical coefficients can be due to the approximate character of these relations and to the difference between the methods used to calculate R_s .¹³⁰

Recall that the parameter D characterises the degree of deformability (mobility) of a macromolecule fragment between chemical cross-linking points. Indeed, an increase in the chain flexibility brings about an increase in C_∞ , *i.e.* an increase in D . It should be noted that extrapolation of straight line $D(C_\infty)$ to $D = 1$ gives $C_\infty \approx 2.55$; evidently, this is the limiting value for epoxy polymers considered. It is also noteworthy that it is close to C_∞ for a linear polymer with a similar structure, for example, for polycarbonate, which has $C_\infty = 2.4$.⁹⁰

Apparently, the deformability of a macromolecule in vitreous epoxy polymers is determined not only by their molecular characteristics but also by supermolecular (supersegmental) 'frozen' structure, which can be characterised quantitatively in terms of the cluster model. It should be borne in mind that an amorphous polymer contains regions of local order (clusters) and that fixing of one or several statistical chain segments in a cluster should change the D value. The most probable reason for the change in D is that the fixed segment becomes expelled from the freely jointed chain, as it has lost its mobility in the junction points. Evidently, this decreases the L_s value in Eqn (39) by l_{st} and, finally, induces a decrease in D . Thus in the case of epoxy polymer EP-1, elimination of one statistical segment induces a decrease in D from 2.06 to 1.73; when two segments are eliminated, D decreases to 1.65; in the case of three segments, it decreases to 1.56, *etc.* In the absence of 'frozen' local order, *i.e.*, for rubbers ($\varphi_{cl} = 0$), $D = 2$ and the loss of chain mobility (deformability) is attained at $\varphi_{cl} \approx 0.65$. The opposite effect is also possible; an increase in v_s induces a decrease in D , *i.e.* the chain becomes more taut, which should increase the level of local order.¹³¹

In the case of linear polymers, the network of macromolecular entanglements is the analogue of the network of chemical bonds; their density V_{en} is determined at $T > T_g$.

Thus, relation (54) is a specific case of a more general fractal relation (57) and is applicable only to rubbers, for which it has actually been derived.

c. Estimation of structural parameters

The cited examples demonstrate the capacity and the prospects of using fractal concepts for the description of macromolecular characteristics of network and linear polymers. The change in the C_∞ value induced by variation of v_s or V_{en} implies that an absolutely different polymer can be formed although the chemical composition of the macromolecule has remained almost the same. This 'new' polymer would have different molecular characteristics (C_∞ , D), a different supersegmental structure (V_{cl} , φ_{cl}), and other properties (glass transition temperature T_g , elasticity modulus E ,

etc.). Equation (54) gives the maximum C_∞ value possible for the given v_s (see Table 6); the minimum values can be obtained by extrapolating the straight line $D(C_\infty)$ to $D = 1$.

At present, vitreous network polymers are mainly characterised by the v_s value.⁴³ However, one network polymer with constant v_s can possess different properties, for example, different glass transition temperatures.¹³² This is explained by the change in the supermolecular structure of a network polymer during physical ageing, namely, by an increase in the level of local order. This effect has been described quantitatively in terms of the cluster model. In turn, the level of local order determines the fractal dimension d_f of the supermolecular (supersegmental) structure of the polymer.⁸ Thus, it becomes possible to predict structural characteristics (and, hence, properties) of network polymers in the vitreous state based on the degree of chemical cross-linking up to the gelation point.

Analysis of the relationship between v_s and d_f for the epoxy polymers considered showed that an increase in the fractal dimension of the framework to the gelation point induces a decrease in the fractal dimension of the supermolecular (supersegmental) structure of the network polymer in the glassy state.

It has been noted in the Introduction that description of fractal structures requires, at least, two dimensions, d_s and d_f , at a constant d value.²⁷ However, the fractal concept is a mathematical model, which does not provide identification of the specific features of the polymer structure. Therefore, in order to use the parameters d_s and d_f in practice (for instance, in computer simulation), one has to find out which elements of the polymer structure (in particular, of network polymers) they embody. It is known⁵⁵ that d_s characterises the degree of connectivity of the framework and d_f (which might be time-dependent) refers to the structure of this framework. The d_f value can be found from Eqn (27), which indicates that d_f is a function only of the Poisson coefficient μ (for fixed d). For amorphous polymers, μ is determined by the degree of local order;⁴⁶ hence, this structural factor also determines d_f . As regards the spectral dimension d_s , it appears to be related in one way or another to the framework formed by chemical cross-links. This suggestion was based on the results of two studies by Kozlov *et al.*^{115, 133} In the former study, the relationships between v_s and the degree of local order and between d_s and d_f were elucidated. The latter study demonstrated the variation of properties of epoxy polymers with time (during physical ageing) following the change in the level of local order (or d_f) with v_s remaining invariant.

The d_s value can be calculated from Eqn (8). For estimating the dimension d_w , needed for this purpose, several relations exist;^{23, 36, 55, 60, 122, 134, 135} they give somewhat different (to within $\sim 20\%$) absolute magnitudes of this parameter. If the variant of constant d_w is chosen and the model of 'lattice animals' ($d = 3$) is used for describing branched polymers, the dependence of d_s on v_s would follow a somewhat unexpected pattern. According to this dependence, an increase in the density of cross-linking points results in lower d_s and, hence, in lower connectivity of the macromolecular framework of chemical cross-links. It is noteworthy that for great v_s , the d_s value approaches asymptotically the experimental spectral dimensions of epoxy polymers.^{22, 35, 69} This finding can be interpreted in terms of the generally accepted models of the structure (or, more precisely, morphology) of network polymers.¹³⁶

The main morphological unit of densely cross-linked epoxy polymers is a globule. It is a local thickening of a molecular space network the packing density in which is higher than the average density. During etching of fractured surfaces of epoxy polymers, this thickening is revealed as a discrete particle — a globule. The non-homogeneity of network polymers is due to both the kinetics of formation of a three-dimensional network and the presence of associates in the initial oligomers.¹³⁶

Two variants of construction of a supermolecular (globular) structure are possible: (a) accrete globules with a hexagonal or cubic packing form a strong continuous skeleton in which the role

of inter-globule defective areas is insignificant; (b) densely cross-linked globules (grains) are located in a sparse-network matrix and do not contact directly one another.

The former variant of morphology seems to be more frequently encountered. An increase in the concentration of a cross-linking agent induces simultaneous generation of a large number of chemical reaction centres; this is confirmed indirectly by a decrease in the size and the increase in the number of globules.¹¹⁶ This results in a smaller size and a greater number of inter-globule defective areas; thus, the connectivity of the skeleton diminishes (defective areas act as sorts of skeletal discontinuities) and, hence, d_s decreases.

In the case where the morphology of a network polymer corresponds to the second variant, its structure can be represented as a mixture of arbitrary polymer fractals in the vicinity of the gelation point; the spectral dimension of the globule is d_s and that of the inter-globule area is δ_s . The δ_s value can be estimated using the relation⁶⁰

$$d_f = d_s \frac{(d+1)(2-\delta_s)}{(2+d_s-2\delta_s)}.$$

As a first approximation, it was assumed in this relation that the spectral dimensions of the structures of the epoxy polymer and the globules are equal. It was found that the dependence of δ_s on v_s for epoxy polymers shows parallel variation of d_s and δ_s upon the variation of v_s provided that $d_s > \delta_s$.⁶⁰ This condition indicates that the skeleton in the inter-globular gaps is less connected than the globules themselves because it is more defective.

Thus, the density of chemical cross-linking points cannot serve as an index for the connectivity of the macromolecular skeleton of network polymers. This makes impossible the use of v_s to characterise the structure of network polymers in a computer simulation, which follows from the results presented above. The d_s value, which provides determination of elastic properties, may serve as a suitable parameter. However, to estimate other properties, one more parameter is required, which would characterise the degree of thermodynamic nonequilibrium of the structures of vitreous polymers. This role can be played by d_f or the density of the cluster network of physical entanglements V_{cl} ,⁴⁷ or by the proportion of clusters ϕ_{cl} .¹³⁷ For instance, the necessity to take into account d_s , V_{cl} or ϕ_{cl} for calculating the yield point from known elasticity modulus has been demonstrated by Beloshenko and Kozlov.⁴⁷ Therefore, the frequently encountered correlations between properties of network polymers and v_s can serve only as an illustration. The use of two parameters (for example, d_s and d_f with a constant d) is a mandatory (fundamental) condition which follows from the fractality of intermolecular frameworks of vitreous polymers; in turn, the fractality is a consequence of thermodynamic nonequilibrium of this structure.

3. Description of molecular mobility using fractal characteristics

The problems of molecular mobility in polymers have always received considerable attention.^{32,95,138} The reasons are obvious — polymers are thermodynamically nonequilibrium solids, their physical properties being determined by molecular relaxation processes occurring in them; these processes, in turn, depend on specific structural features of molecular chains and the structural organisation of polymers.¹³⁸ However, there is no consensus regarding the parameters describing these processes. In particular, it is assumed that fast relaxations are determined by the mobility of free chains located between densely packed regions, which are simultaneously the nodes of the network of physical entanglements in a macromolecule. This interpretation fully complies with the main statements of the cluster model for the structure of amorphous polymers,¹⁵ which provides quantitative description of structural elements. The relationship between the cluster model and fractal analysis can be formulated as follows: fractal analysis gives general physical parameters, while

the cluster model makes them more specific using particular characteristics of polymers.

Yet another important aspect is worth noting. The above interpretation of the structure of amorphous polymers refers to elastomers. Extension of these notions to vitreous amorphous polymers implies 'freezing' of densely packed regions, *i.e.* a sharp increase in their lifetimes. The fractal forms of macromolecules, macromolecular coils formed during nonequilibrium physico-chemical processes are retained (remain 'frozen') in polymers. This suggests that the main factor determining the molecular mobility in the vitreous state is the mobility of chain fragments between the points of fixing.¹¹¹

The fractal dimension D has been chosen as the structural factor characterising the level of molecular mobility;¹¹¹ this was done for the following reasons. First, a chain fragment between the points of fixing is a self-similar object having a dimension differing from the topological dimension, *i.e.* it is a fractal by definition.¹⁰⁷ Second, it was shown¹⁰¹ that D with the range of variation $1 < D \leq 2$ characterises exactly the molecular mobility of a chain fragment in loosely packed regions.¹³⁸ The condition $D = 1$ implies stretching of this chain fragment and loss of fractal properties and mobility. In terms of relaxation spectroscopy, this means that $\tan \delta = 0$, where $\tan \delta$ is the mechanical (or dielectric) loss tangent. The condition $D = 2$ means the maximum possible mobility of the chain section, which corresponds to a rubbery state of the polymer, *i.e.* it is consistent with the maximum value of $\tan \delta$ at the glass transition temperature T_g .

Figure 15 shows the dependence of $\tan \delta$ on D for several copolymers¹¹¹ [the D values were calculated using Eqn (48)] for a measurement frequency of 1 kHz. The dependence has clearly defined limits. For $D = 1$, it is extrapolated to $\tan \delta = 0$. When $D = 2$, $\tan \delta$ is roughly equal to the corresponding value at T_g . Thus, linear dependences with the limiting $\tan \delta$ values indicated above can be used to predict the fractal dimension.

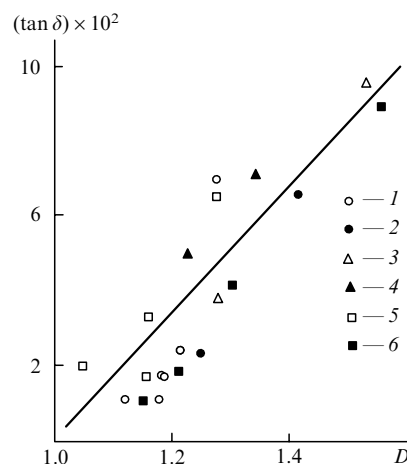


Figure 15. Dielectric loss tangent $\tan \delta$ vs. fractal dimension D of the macromolecule section for copolyethersulfoneformals with the content of formal blocks of 0 (1), 5 (2), 10 (3), 30 (4), 50 (5) and 70 (6) mol.%. Measurement frequency 1 kHz.¹¹¹

Now we shall consider examples of using the dimension D for the solution of applied problems. When polymer samples are obtained by solid-phase extrusion, the macroscopic (extrusion) draw ratio λ_e is determined by the ratio^{119,139,140}

$$\lambda_e = \frac{\phi_b^2}{\phi_{spin}^2}, \quad (60)$$

where ϕ_b , ϕ_{spin} are the diameters of the billet and the spinneret, respectively.

However, the structure and properties of oriented polymers are characterised much more adequately by the molecular draw

ratio λ_{mol} .¹²² The following expression relating λ_e , λ_{mol} and D to one another has been obtained:¹²⁰

$$\lambda_{\text{mol}} = \frac{l_{\text{st}} \lambda_e^{2/D}}{R_s}. \quad (61)$$

It follows from this relation that the lower D , *i.e.* the more 'frozen' the molecular mobility of the chain during drawing, the greater λ_{mol} (the more efficient the orientation process), all other factors being the same.

The limiting draw ratio λ_{∞} attained by stretching a polymer is determined, in terms of the rubbery high-elasticity theory, by the equality¹²¹

$$\lambda_{\infty} = n_{\text{st}}^{1/2}, \quad (62)$$

where n_{st} is the number of statistical segments.

This equation has been applied repeatedly to vitreous polymers. The following fractal relation has been obtained:³⁸

$$\lambda_{\infty} = n_{\text{st}}^{D/4}. \quad (63)$$

It can be easily seen that an increase in D for $n_{\text{st}} = \text{const}$ enhances the deformability of polymers. Equations (62) and (63) are identical when $D = 2$, *i.e.* for rubbers.

An important difference between Eqns (62) and (63) is that in the former, λ_{∞} depends on one parameter, which is typical of equilibrium Euclidean objects, while in the latter, it is a function of two parameters, which is typical of thermodynamically nonequilibrium fractal objects. Therefore, the use of Eqn (62) in the latter case is improper.

The relationship between the statistical chain flexibility, characterised by C_{∞} , and the dimension D has been found¹⁴¹

$$D = 2 - \frac{1}{C_{\infty}}. \quad (64)$$

Using published data for C_{∞} (see, for example, Ref. 90) and Eqns (27) and (49), the lengths of chain sections between entanglements L_{en} were calculated. The results were in agreement with experimental data (Table 7). Thus, the increase in the density of the network of macromolecular entanglements following an increase in the statistical chain rigidity was confirmed within the framework of fractal analysis. By combined use of Eqns (27) and (49), one can predict the increase in the number of points of topological fixing of a macromolecule in the vitreous state with respect to the rubbery state.¹⁴¹

The fractal dimension D of a chain fragment between the points of topological fixing (entanglements, clusters, cross-links) is an important structural parameter, which controls the molec-

ular mobility and deformability of polymers. Crucial factors accounting for the use of the dimension D are clearly defined limits of variation ($1 < D \leq 2$) and dependence on the supermolecular structure of the polymer. It should be emphasised that all fractal relations contain at least two variables. Therefore, correlations between some property of polymers and the density of the network of entanglements (cross-links), which are frequently encountered in the literature, can serve only as illustrations. The necessary use of at least two parameters (for instance, d_s and d_f with a constant d) is a fundamental condition, which follows from the fractality of the intermolecular skeletons in vitreous polymers.

IV. Conclusion

The fractal properties of a macromolecule in a polymer are predetermined by thermodynamic nonequilibrium and by the presence of a certain deterministic order. Proceeding from this fact, we considered the limitations of the scope of the concept of polymer fractal, developed for polymer solutions, and the Vilgis theory for condensed media (melts and rubbers). The major drawback of these approaches is that they neglect the effects of macromolecular entanglements. It is demonstrated that a description of the fractal properties of macromolecules cannot be physically correct without allowance for entanglements. Examples are given to illustrate the diversity of fractality in polymers. In particular, it is shown that not only macromolecular coils but also sections of macromolecules between the points of topological fixing (cross-links, entanglements) are stochastic fractals.

Conditions required for the fractality to be manifested are discussed. They include the range of scales, self-similarity and fractional dimension. It is shown that a section of a macromolecule between the points of topological fixing possesses configurational fractal properties, caused by the mutual arrangement of fragments of the macromolecule, and conformational fractal properties, conditioned by the state of bonds within a section of rigidity (*i.e.* statistical segment). In this connection, a model of structure formation in network polymers is considered; this model includes a quantitative determination of the relationship between the cross-linking density and the level of local order of the structure. It is demonstrated that, in addition to the parameters of local order, fractal dimensions of the polymer structure should also be taken into account. Examples of practical use of the fractal dimension of the section of a macromolecule between chemical cross-linking points are given; it is shown that this value can serve as a measure of molecular mobility. The influence of characteristics of molecular and topological levels of the structure of cross-linked polymers on the fractal dimension is noted.

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Table 7. Characteristic ratios C_{∞} and L_{en} .¹³¹

Polymer	C_{∞} ^{90, 132}	L_{en} / nm	
		experiment	calculation
Poly(n-dodecyl methacrylate)	13.4	226	208
Poly(n-octyl methacrylate)	10	177	149
Polystyrene	10	104	149
Poly(vinyl acetate)	9.4	88	136
Poly(n-butyl methacrylate)	9.1	130	131
Poly(methyl methacrylate)	8.6	97	92
Polyethylene	6.8	56	88
Poly(vinyl chloride)	6.7	31	87
Polytetrafluoroethylene	6.3	41	80
Polyamide-6	5.3	46	61
Poly(propylene oxide)	5.1	60	58
Poly(ethylene oxide)	4.2	45	43
Poly(ethylene terephthalate)	4.2	21	36
Polyetherterephthalate	3.3	28	30
Polycarbonate	2.4	29	17

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^b — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*

^c — *Physics-Uspekhi (Engl. Transl.)*

^d — *Polym. Sci. (Engl. Transl.)*

Sulfones and sulfoxides in the total synthesis of biologically active natural compounds

E N Prilezhaeva

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Abstract. Data on the use of sulfones and sulfoxides in total stereo-, regio- and enantioselective syntheses of natural compounds published over the last 15–20 years are discussed and classified into the most important types of reactions. The bibliography includes 420 references.

I. Introduction

Sulfonyl- and sulfinyl-containing intermediates and their precursors are finding increasing use in the synthesis of natural compounds because these groups satisfy the requirements of sophisticated multistage transformations. In this review, the most important requirements are stated based on the concepts proposed by the eminent chemist and populariser of science, E Block.¹

These functional groups should be:

- (1) readily accessible;
- (2) highly reactive;
- (3) able to effect asymmetric induction;
- (4) readily removable at a particular stage of the synthesis.

Sulfoxides and sulfones are rather readily available compounds. Methods for their synthesis both from the corresponding sulfides and other precursors have been well developed.^{2–5}

Owing to their high reactivity, sulfoxides and sulfones can induce the stereo-, regio- and enantioselective formation of new C–X bonds and, what is particularly important, of C–C bonds.

Enantiomerically pure sulfoxides are excellent mediators in the asymmetric synthesis. The fact that the sulfur atom in sulfoxides containing different substituents is an ideal asymmetry center (Montanari⁶ was the first to note this fact back in the 1970s) is not the only reason. The ability of the sulfinyl group to form chelates due to complexation with other polar groups in the molecule as well as with catalysts is used in enantioselective syntheses resulting in 1 → 2, 1 → 3 and more distant asymmetry

transfer.^{5,7–13} The wide application of chiral sulfoxides is also favoured by the availability of convenient methods for their preparation in enantiomerically pure *S*- or *R*-forms.^{5,12}

Sulfonyl groups do not possess inherent asymmetry and are substantially less active complex-forming agents. However, due to their specific bulk and electronic properties, these compounds can perform regio- and stereocontrol. Reactions of sulfones proceed under rather mild conditions, which makes it possible to retain chiral carbon centres (even those located in the vicinity of the sulfonyl group) throughout the process.

A wide variety of chemoselective procedures for the removal of sulfonyl and sulfinyl groups are available (see, for example, Ref. 14). Classical heterogeneous reduction with Raney nickel (Ra/Ni) continues to be used. Mild heterogeneous desulfonation (desulfination) with metal amalgams (primarily with Na/Hg) is also often employed. However, the majority of modern procedures involve homogeneous processes, *viz.*, reactions of transition metal salts, palladium(0) complexes or solutions of alkali metals in ammonia. Since the use of lanthanides have attracted growing interest in recent years,^{15,16} mild desulfonation with SmI₂ is rather often used (see, for example, Refs 16–19). Reductive desulfurisation, elimination of sulfenic and sulfinic acids to form C=C bonds and double elimination of hydroxy and sulfonyl groups from substituted sulfones can readily be performed. Although the sulfonyl fragment is a poor leaving group (see, for example, Ref. 20), conditions were found under which this group in some compounds can be replaced by the attacking reagents.

In spite of the fact that synthetic applications of sulfones have been surveyed (see, for example, Refs 21 and 22), the data on the use of these compounds in the synthesis of natural products remain to be systematised. Applications of particular types of sulfones, such as γ -hydroxyvinyl sulfones^{23,24} and sulfolenes,^{25,26} for these purposes have been described. Examples of the use of sulfones were cited in reviews devoted to syntheses of selected groups of natural compounds (juvenile hormones²⁷ and linear polyprenols^{28,29}). Recently, Carreno¹² has reported a comprehensive analysis of the uses of chiral sulfoxides in asymmetric syntheses of biologically active compounds. Therefore, in the present review the attention is focused on sulfonyl-containing and racemic sulfinyl-containing precursors and intermediates without special reference to asymmetric synthesis, all the more so since the stereochemistry of all chiral centres has not always been reported in the original studies. Yet another aim of this review is to

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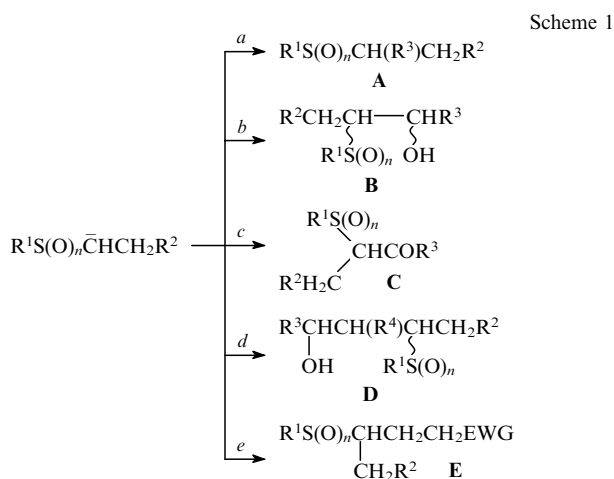
Uspekhi Khimii 69 (5) 403–446 (2000); translated by T N Safonova

demonstrate how successfully sulfones and sulfoxides complement each other in syntheses of natural compounds.

II. Brief characterisation of reactions applicable in the synthesis of natural compounds based on the use of sulfones and sulfoxides

Even a brief analysis of reactions of sulfoxides and sulfones gives an idea of their wide synthetic potential. These compounds can provide the basis for the erection of the building for the synthesis of natural compounds. Fuchs and coworkers²⁴ compared this building to a majestic pyramid.

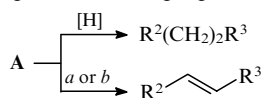
Reactions of carbanions stabilised by α -sulfonyl or (to a lesser extent) α -sulfinyl groups are often used in the synthesis of natural compounds. Among various reagents used for α -deprotonation,^{30, 31} lithium bases (for example, alkyllithium compounds or lithium diisopropylamide LDA) predominate. In this review, these species will be sometimes described as C-lithiated species in accordance with the original reports although this is not quite correct. It has been rigorously proved³² that in the crystalline state of sulfur-containing alkyllithium compounds, the metal atom is bound to the oxygen atom of the sulfonyl (sulfinyl) group rather than to the α -carbon atom. However, this fact is not reflected in their reactions in solution. Electrophilic reagents attack exclusively the carbon atom unlike their reactions with carbanions stabilised by the carbonyl group. Alkylation with alkyl or cycloalkyl halides, tosylates or mesylates (Scheme 1, path *a*) affords



$n = 1, 2$; (a) R^3X , $X = \text{Hal, OTs, OMs}$ ($\text{Ms} = \text{MeSO}_2$); (b) $R^3\text{CHO}$;

(c) $R^3\text{CO}_2R^4$; (d) R^3 -oxirane- R^4 ; (e) CH=EWG , EWG is an electron-withdrawing group.

sulfones or sulfoxides **A** and their reductive desulfurisation leads to the elongation of a saturated chain. Elimination of fragments of acids RSO_nH ($n = 1$ or 2) from derivatives **A** results in the formation of the $\text{C}=\text{C}$ bond. For most sulfones, this process occurs under rather drastic conditions. Many sulfoxides eliminate sulfenic acid upon mild thermolysis, which provided the basis for a method of introduction of $\text{C}=\text{C}$ bonds with *E* configuration into complex molecules proposed by Trost.^{33–35}



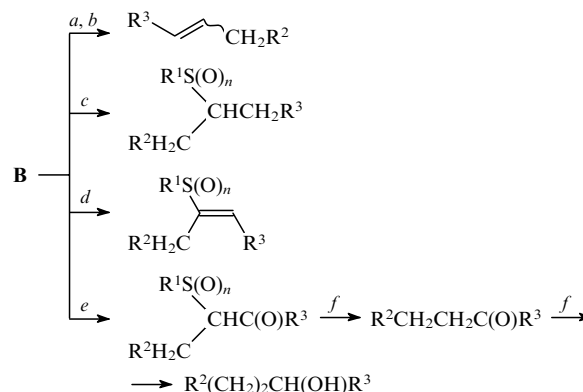
(a) $n = 2$, **B**•; (b) $n = 1$, Δ .

Reactions with carbonyl compounds or oxiranes lead to the 1,2-addition at the carbonyl group (Scheme 1, paths *b* and *c*) or to the oxirane-ring opening (path *d*). Reactions of α -sulfonyl carbanions with aldehydes are of particular importance because the

resulting epimeric mixtures of 2-hydroxy sulfones **B** ($n = 2$) serve as an inexhaustible source for the construction of new functional groups, viz., vinylsulfonyl, oxosulfonyl, saturated hydroxy or oxo groups.

Of prime importance is the Julia olefination resulting in stereoselective construction of the $\text{C}=\text{C}$ bond with either the *E* (Ref. 36) or *Z* (Ref. 37) configuration following acylation of the hydroxy group (Scheme 2, paths *a* and *b*).

Scheme 2



(a) $n = 2$, Ac_2O ; (b) Na/Hg ; (c) $n = 1, 2$; (d) $n = 2$, **B**•; (e) $n = 2$, $[\text{O}]$; (f) $[\text{H}]$.

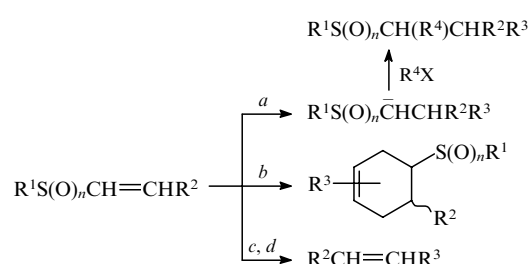
The most important precursors in the asymmetric synthesis, viz., 2-hydroxy sulfoxides (**B**, $n = 1$),¹² must be used only in enantiomerically pure form. Therefore, these compounds are generally prepared by selective reduction according to Solladie^{38, 39} starting from 2-oxo sulfoxides **C**. The most convenient procedure for the synthesis of the latter involves the reaction of α -sulfinyl carbanions with the carbonyl groups of esters (Scheme 1, path *c*).

α -Sulfonyl(sulfinyl) carbanions, being active C-nucleophiles, readily react with various electron-deficient multiple bonds (Scheme 1, path *e*).

Either aryl or (more rarely) *tert*-butyl groups generally serve as substituents R^1 in sulfonyl(sulfinyl) fragments. This is dictated not only by the necessity of providing conditions for regiospecific deprotonation but also for kinetic reasons. For example, benzenesulfenic acid is eliminated upon thermolysis of sulfoxides at substantially lower temperatures than methanesulfenic acid.⁴⁰

Among unsaturated precursors, vinyl sulfones are worthy of particular attention. Fuchs and coworkers^{23, 24} believed that these sulfones are ideal starting compounds (superior even to enones) for sophisticated syntheses. New $\text{C}-\text{C}$ bonds are formed upon addition of C-nucleophiles (predominantly metal alkyls) at the activated $\text{C}=\text{C}$ bonds of vinyl sulfones followed by the reaction of electrophiles with the resulting α -sulfonyl carbanionic centre (Scheme 3, path *a*). Reactions of the $\text{C}=\text{C}$ bonds of ene sulfoxides with C-nucleophiles occur successfully, if additional acceptors, for example, carbonyl groups, are introduced into the sulfoxide molecules. Reactions of heteronucleophiles with ene sulfoxides

Scheme 3



$n = 1, 2$; (a) R^3M ($M = \text{Li, MgX}$); (b) $\text{CH}_2=\text{CH}-\text{C}(=\text{O})-\text{R}^3$; (c) $n = 2$, $R^3\text{MgX}$, Ni(II) or Fe(III) ; (d) **B**•.

and ene sulfones (see Section V.1.b) as well as the Diels–Alder [4 + 2] cycloaddition (Scheme 3, path *b*) are also widely used. Cross-coupling of vinyl sulfones with Grignard reagents in the presence of transition metal salts makes it possible to replace the sulfonyl group according to Julia,⁴¹ the C=C bonds being unaffected (Scheme 3, paths *c* and *d*).

Linear and cyclic polyunsaturated structures are successfully constructed with the use of various 1,3-dienes generated from substituted 3-sulfolenes by cheletropic elimination of SO₂.²⁶

Allyl sulfoxides and, particularly, allyl sulfones are very reactive compounds. Due to abstraction of the labile allylic hydrogen, these compounds readily form ambident carbanions, which can undergo alkylation both at the α - and (more rarely) γ -positions. In the presence of palladium catalysts or Lewis acids, the sulfonyl group in allyl sulfones is replaced by various nucleophiles.^{42,43} Because of the wide diversity of their transformations, Trost⁴⁴ has named allylic sulfones ‘organic chameleons’.

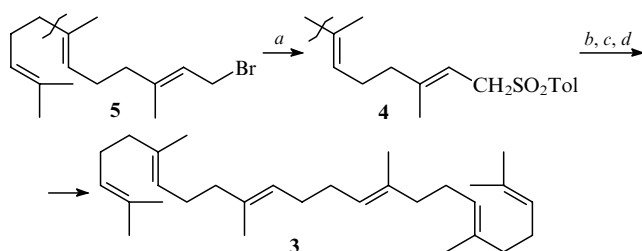
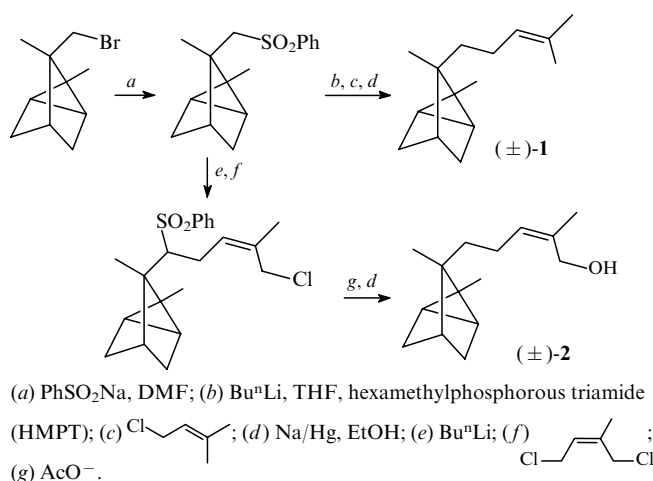
Of rearrangements of sulfoxides and sulfones, the Mislow–Evans sulfinyl–sulfenate rearrangement^{45,46} (which is used for the formation of hydroxy allylic fragments), the Pummerer reaction^{47,48} (which has many applications, but is predominantly used for the construction of cyclic molecules) and the Ramberg–Bäcklund reaction^{49,50} (which is used for the introduction of C=C bonds) are most commonly used in the synthesis of natural compounds. Because of a great body of information on syntheses involving rearrangements of sulfoxides and sulfones, these processes cannot be considered in this review in detail.

III. Syntheses based on α -sulfonyl or α -sulfinyl carbanions

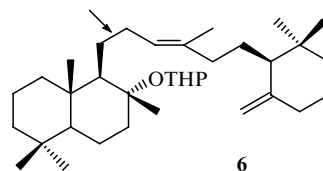
1. Alkylation

a. Alkylation followed by reductive removal of sulfur-containing groups

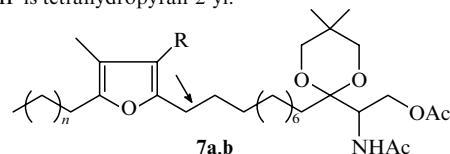
The simplest procedure for the formation of new C–C bonds involves alkylation of α -sulfonyl or α -sulfinyl carbanions followed by reductive removal of sulfur-containing groups. This strategy was used for the first time in the syntheses of components of essential oils, *viz.*, racemic α -santalene [($\pm$)-**1**] and α -santalol [($\pm$)-**2**],⁵¹ as well as for the preparation of a pure *trans*-isomer of



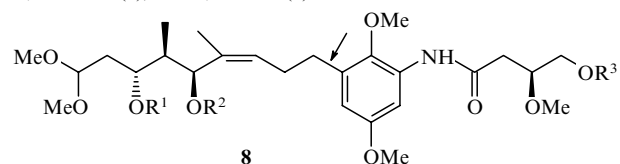
squalene (**3**)⁵² by alkylation of the anion of farnesyl phenyl sulfone (**4**) with farnesyl bromide (**5**). This procedure is often used for the coupling of complex polyfunctional fragments containing numerous chiral centres. Recently, this method has been used for the preparation of intermediates **6–8** in the synthesis of ambrein (the intermediate **6**⁵³), polysubstituted biologically active furan compounds, *viz.*, calicogorgins A and C (the intermediates **7a** and **7b**, respectively⁵⁴), and the antibiotic mycotrienin (the intermediate **8**⁵⁵) (the sites of coupling are indicated by arrows).



THP is tetrahydropyran-2-yl.

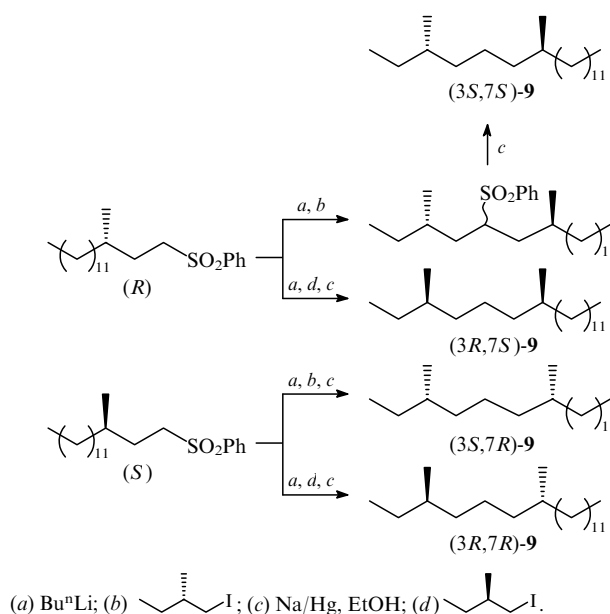


$n = 1$, R = Me (**a**); $n = 2$, R = H (**b**).



R¹–R³ are protective groups.

This procedure can also be used for the construction of linear enantiomerically pure pheromones, both saturated and containing isolated C=C bonds. Mori and coworkers^{56–64} performed convergent syntheses of pheromones (*ee* 97%–98%) starting from two or more enantiomerically pure building blocks. If the absolute configuration of the natural pheromone was unknown, all possible enantiomers were synthesised in amounts sufficient for biological assays. Below are presented the syntheses of four possible enantiomers of 3,7-dimethylnonadecane (**9**), which is a pheromone of tortricid *Agromyza frontella* (an alfalfa pest).⁵⁶



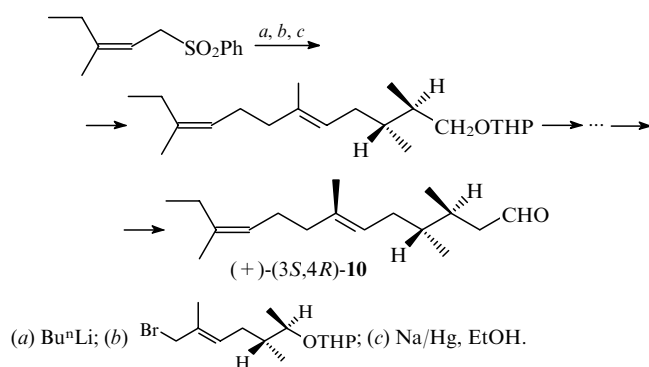
Other pheromones synthesised by Mori and coworkers with the use of alkylation–desulfonylation methodology are listed in Table 1 (the coupling sites are indicated by arrows).

Table 1. Pheromones synthesised by alkylation–desulfurisation.

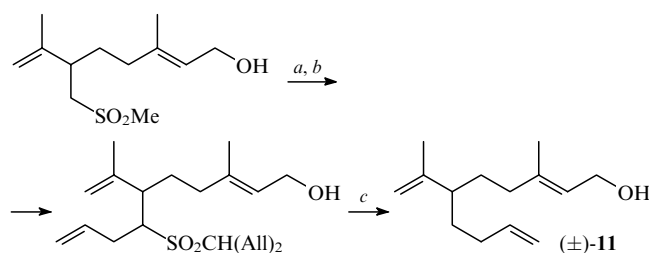
Name	Structure	Absolute configuration of natural pheromone	Biological characteristic	Number of possible enantiomers (the number of enantiomers synthesised)	Ref.
13,17-Dimethyl-nonatriacontane		unknown	kairomone for wasp <i>Trichogramma nubiale</i>	4 (4)	57
3,13-Dimethyl-heptadecane		"	sex pheromone of western false hemlock looper <i>Nepytia freemani</i>	4 (4)	63
6,10,14-Trimethyl-pentadecan-2-ol		(2 <i>R</i> ,6 <i>R</i> ,10 <i>R</i>) ^a	pheromone of rice moth <i>Corcyra cephalonica</i>	8 (8)	58
6,10,13-Trimethyl-tetradecan-1-ol		unknown	aggregation pheromone of predatory stink bug <i>Stiretrus anchorago</i>	4 (4)	59
6,12-Dimethyl-pentadecan-2-one		"	female-produced sex pheromone of banded cucumber beetle <i>Diabrotica balteata</i> Le Conte	4 (4)	60
4,8-Dimethyldecanal		(4 <i>R</i> ,8 <i>R</i>)	aggregation pheromone of red-flour beetle <i>Tribolium castaneum</i>	4 (2) ^b	61
Methyl 2,6,10-trimethyltridecanoate		unknown	sex pheromone of stink bug <i>Euschistus heros</i> / <i>E. obscurus</i>	8 (8)	62

^a Preliminary data of biological studies. ^b In the study,⁶¹ enantiomers inactive with respect to *Tribolium castaneum*, but active with respect to other species *Tribolium* were prepared.

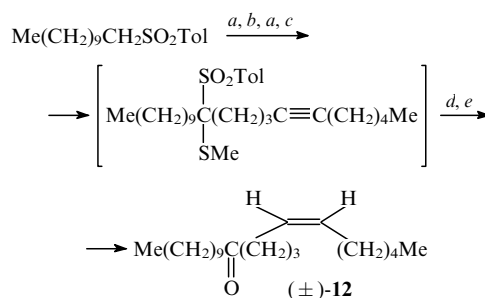
Pheromones whose molecules contain double bonds were constructed by alkylation–desulfonation starting from allylic sulfones and (or) allylic halides. This procedure was used for the preparation of enantiomerically pure faranal (**10**), which is the pheromone of Pharaoh's ant.⁶⁴



The synthesis of the pheromone of California scale (±)-**11** in the racemic form required the use of a threefold excess of allyl bromide because deprotonation and, correspondingly, alkylation of the initial methyl sulfone occurred non-regiospecifically.⁶⁵



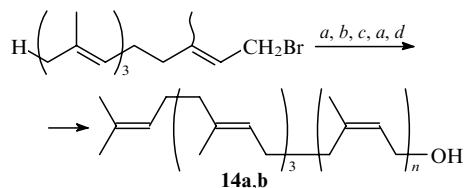
In the synthesis of the sex pheromone of Douglas fir tussock moth **12**, α-thiolation followed by hydrolysis was used for the simultaneous formation of the oxo group and removal of the sulfonyl group; the C=C bond was formed by stereospecific hydrogenation of the triple bond.⁶⁶



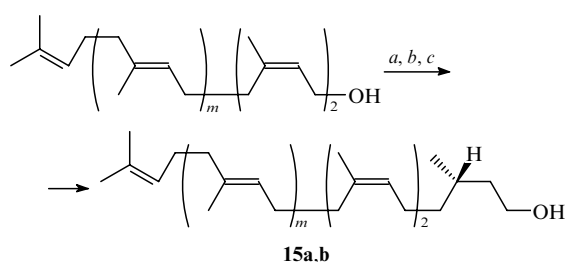
(a) BuⁿLi; (b) 2 equiv. of Me(CH₂)₄C≡C(CH₂)₃I; (c) (MeS)₂; (d) CuCl₂, SiO₂; (e) H₂, 5% Pd/BaSO₄.

An elegant method for stepwise alkylation developed by Moiseenkov and coworkers^{28, 67–70} makes it possible to synthesise polyunsaturated natural molecules by C₅-homologation. Lithiated δ-hydroxyallylic or saturated sulfones (including those containing a chiral centre) and the corresponding unsaturated terpenoid halides served as the starting compounds. This methodology was used for the preparation not only of relatively small molecules [for example, the pheromone components of San-Jose scale, viz., α-neryl and α-geranyl propionates (**13a,b**)⁶⁷], but also of long-chain natural regulators, such as polyphenol- and dolichol-like alcohols **14**⁶⁸ or **15**.⁶⁹ The addition of a crown ether, viz., dibenzo-18-crown-6 (DB-18-C-6), to a solution of sodium in liquid ammonia in the stage of reductive desulfonation made it

DB-18-C-6; (c) EtCOCl.



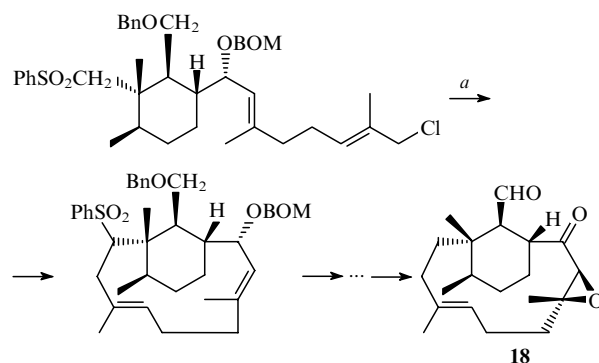
(d) Na/NH₃, DB-18-C-6.



$m = 2$ (**a**), 3 (**b**); (a) PBr_3 ; (b) $\text{PhSO}_2\text{CHLi} \begin{array}{c} \text{Me} \quad \text{H} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \text{CH}_2\text{CH}_2\text{OLi}$; (c) Na/NH_3 .

Chemical reaction scheme showing the synthesis of (±)-16. The starting material is a substituted piperidine derivative with a PhSO_2 group, an OTs group, a Boc group, and a Pr^n group. It reacts with reagent a to form an intermediate bicyclic structure with a PhSO_2 group and a Boc group. This intermediate then undergoes two more steps to yield the final product, (±)-16, which is a bicyclic amine with a methyl group and a Pr^n group.

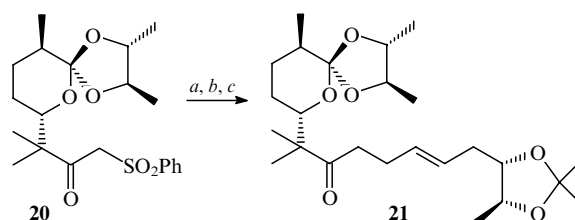
(a) BuⁿLi, THF, -78 °C; (b) Me₂CuLi, Et₂O, Me₂S; (c) Na, EtOH, THF.



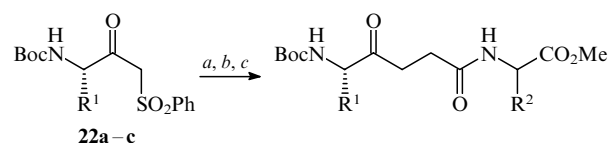
Chemical reaction scheme showing the synthesis of compound **19**. The starting material is a complex bicyclic molecule with a BnOCH_2 group, a BnO group, a SO_2Ph group, and an iodide. It is converted to an intermediate bicyclic compound with a CH_2OBn group, a BnO group, and a SO_2Ph group via step (a). The intermediate is then converted to compound **19**, which is a bicyclic molecule with a CH_2OH group and a HO group, via steps (b) and (c).

the enantiomerically pure form starting from (*S,S*)-(–)-diethyl tartrate,⁷² phomactin D (**18**), which is a 12-membered PAF antagonist,⁷³ and the 14-membered carbocycle 7(8)-deoxyasperdiol (**19**), which is a synthetic precursor of the widespread membranoid antitumor agent asperdiol.⁷⁴

Intramolecular alkylation was used in the total synthesis of 21-membered heterocyclic antibiotics (+)-trienomycins A and F⁷⁶ and for the construction of the *AB* ring system of taxol.⁷⁷



(a) BuⁿLi, DMSO, KI; (b) ; (c) Al/Hg, EtOH.



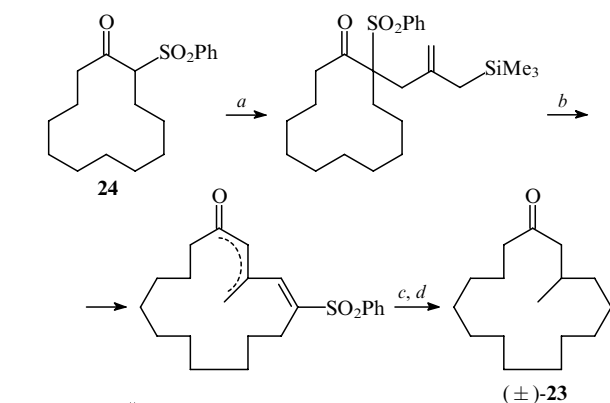
(b) ; (c) SmI₂, THF, MeOH, -78 °C,

20 min (50%–98%).

Unlike the above-mentioned studies in which alkylation was generally performed with the use of bromides or iodides, the enantiomerically controlled construction of the C(1)–C(17) fragment in the total synthesis of ionophoric boromycin was carried out using the mild reaction of a chloride with an anion generated from the 2-oxosulfonyl group.⁷⁸

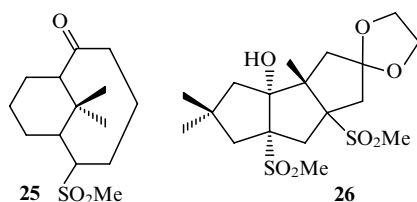
Oxo sulfone **20** serves as an example of additional activation of the α -sulfonyl carbanionic centre in alkylation. The sulfone **20** was used as the starting material in the synthesis of compound **21**, which is the key intermediate for the preparation of the antibiotic ($\pm$)-aplasomycin.⁷⁹ Amino-acid-derived oxo sulfones **22a–c** were successfully used in the peptide synthesis.⁸⁰

Cyclic ketones containing the sulfonyl group at the α -position undergo three-carbon ring expansion when a fluoride anion acts on the products of alkylation of enolates of these ketones with silicon-containing allylic iodides or mesylates [$\text{Me}_3\text{SiCH}_2(\text{XCH}_2)\text{C}=\text{CH}_2$], which generate trimethylenemethane.⁸¹ Trost and coworkers⁸² used this procedure for the preparation of muscone **23** from 2-sulfonylcyclododecanone **24** in high yield.

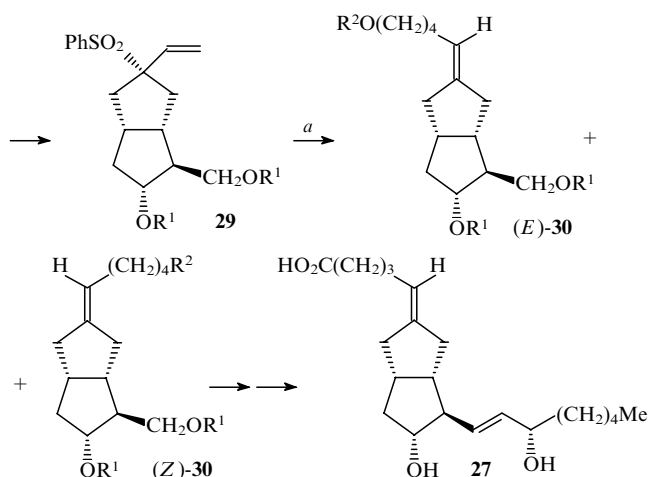
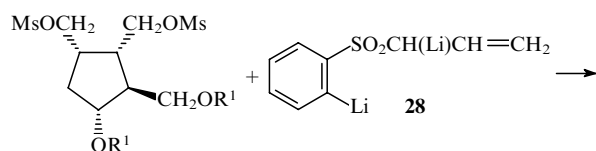


(a) $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{X}$ (X = I, OSO₂Me), NaH, NaI, DME;
(b) $\text{Bu}_4\text{N}^+\text{F}^-$, THF; (c) H_2 , 5% Pd/BaSO₄; (d) Na/Hg, Na₂HPO₄, H₂O.

The application of more complex oxosulfonyl precursors made it possible to construct sterically hindered systems of the 11,11-dimethylbicyclo[5.3.1]undecane series, such as compound **25**, which is the key intermediate in the synthesis of taxane derivatives,⁸³ as well as to prepare fused cyclopentanoids of the type **26**, which serve as the starting compounds for the preparation of hirsutene, hirsutic acid and coriolin.⁸⁴



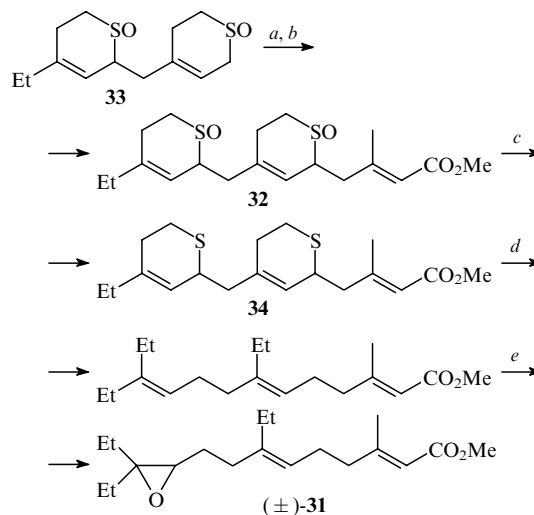
The formal total synthesis of carba-prostacyclin (**27**), which is an analogue of prostacyclin, was reported.⁸⁵ The compound **27** is more stable, but exhibits no lesser activity in the inhibition of blood coagulation. The allylic sulfone dianion **28** was alkylated with enantiomerically pure mesylate of substituted hydroxycyclopentane. The necessary side chains were introduced into compound **29** by reactions with the corresponding lithium cuprates. The reactions were accompanied by the replacement of the



R¹ = SiMe₂Bu^t; (a) LiCu[(CH₂)₃OR²]₂; R² = CH(Me)OEt.

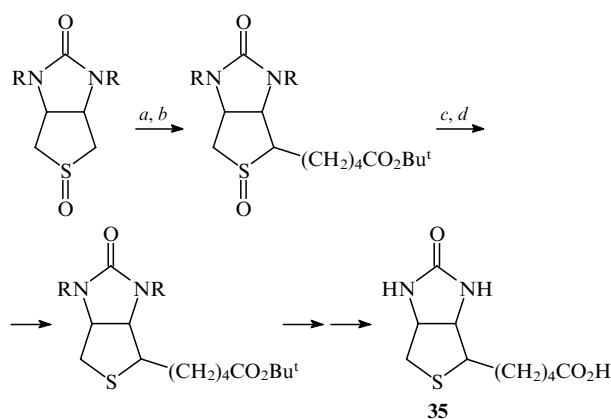
sulfonyl group and migration of the C=C bond to form a mixture of (*Z*)- and (*E*)-isomers of compound **30**. The latter is the key intermediate in the synthesis of carba-prostacyclin (**27**).

As to α -sulfonyl carbanions, the simplest alkylation–reductive desulfonylation procedure is rather rarely used in the synthesis of natural compounds. However, the racemic juvenile hormone **31** was synthesised by two-step reduction of the compound **32**, which is an alkylation product of disulfoxide **33**, via intermediate dithioether **34**.⁸⁶



(a) LDA; (b) BrCH₂CH=CHCO₂Me; (c) SnCl₂, AcCl, DMF;
(d) Ra/Ni, DMSO; (e) *m*-chloroperbenzoic acid (MCPBA).

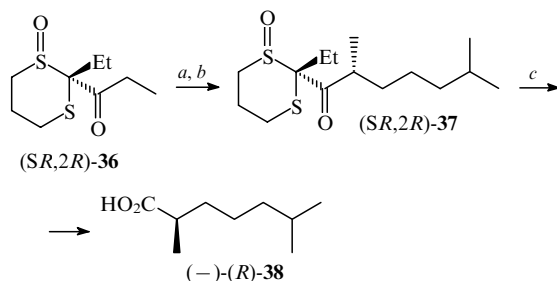
In the total synthesis of racemic biotin **35**,⁸⁷ an intermediate obtained by alkylation of a sulfoxide was reduced to sulfide.



R = Bn, All; (a) MeLi; (b) I(CH₂)₄CO₂Bu^t; (c) TiCl₃; (d) HBr.

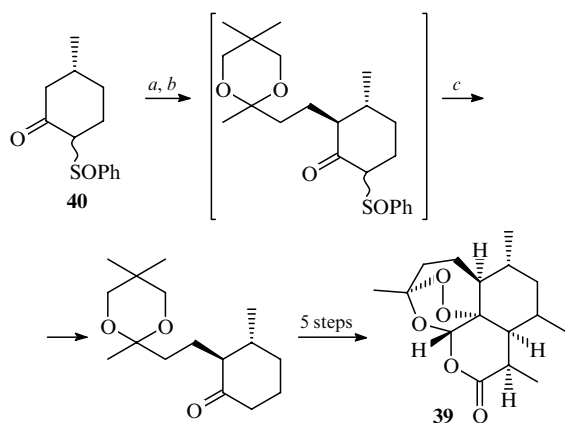
Deprotection of the amino and carboxy groups was performed in two steps to produce ($\pm$)-biotin **35**.

The reactions given below exemplify the use of alkylation of the anions derived from oxo sulfoxides upon deprotonation at the α -position with respect to the carbonyl group. Due to the induction exerted by the sulfinyl group, alkylation of an enantiomerically pure derivative of 1,3-dithiane 1-oxide (**36**) proceeded selectively to form compound **37**. Its hydrolysis afforded natural (–)-(*R*)-2,6-dimethylheptanoic acid [(–)-(*R*)-**38**].⁸⁸



(a) $(\text{Me}_3\text{Si})_2\text{NLi}$; (b) 1-iodo-2,6-dimethylheptane; (c) NaOH (39%).

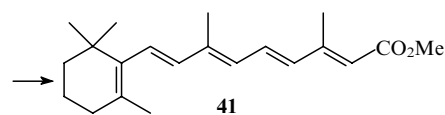
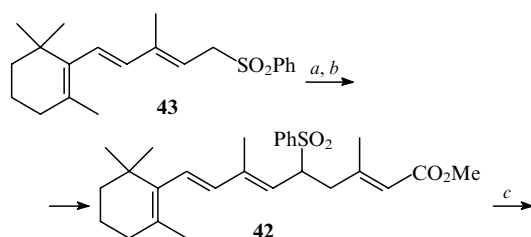
The total synthesis of an antimalarial drug, viz., sesquiterpenoid (+)-artemisinin (**39**), was carried out starting from sulfoxide **40**,⁸⁹ which had been prepared from pulegone. The sulfinyl group acts as an activating agent that promotes alkylation of enolate.



(a) 2 equiv. of LDA, HMPT, THF, -35°C ; (b) bromo-ether intermediate; (c) Al/Hg.

b. Alkylation of α -sulfonyl carbanions followed by elimination of sulfinic acid

Homoallylic sulfones are promising starting compounds for the introduction of C=C bonds by alkylation of α -sulfonyl carbanions followed by elimination of sulfinic acid. Julia and Arnould⁹⁰ were the first to use this approach in the synthesis of natural compounds. These authors performed a convergent ($\text{C}_{15} + \text{C}_5$)-synthesis of methyl retinoate (**41**) related to vitamin A starting from β -ionone. The key step of this scheme involves dehydrosulfinylation of homoallylic sulfone **42** prepared by alkylation of



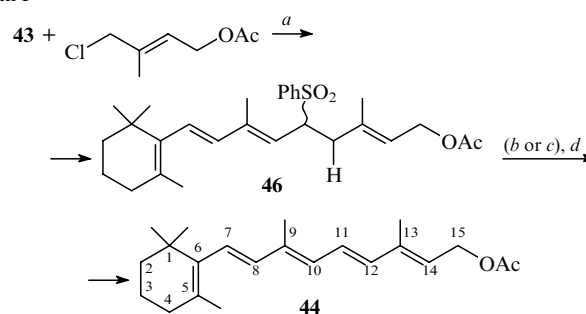
(a) Bu^nLi ; (b) Br-ether intermediate; (c) K_2CO_3 , MeOH (73%).

sulfone **43**. However, the *E*-configurations of all C=C bonds of the final reaction product **41** have not been established reliably.⁹⁰

This study⁹⁰ gave impetus to intensive investigations aimed at developing a sulfonyl procedure for the preparation of vitamin A as retinol acetate (**44**) (the results were surveyed in Ref. 91). This approach seemed to be promising owing to a small number of steps and the possibility of recycling of the sulfinate eliminated. The most essential results were obtained by researchers of Rhone–Poulenc^{92,93} and of Hoffman–LaRoche.^{94,95} Two versions of the convergent ($\text{C}_{15} + \text{C}_5$) schemes (Scheme 4, paths I

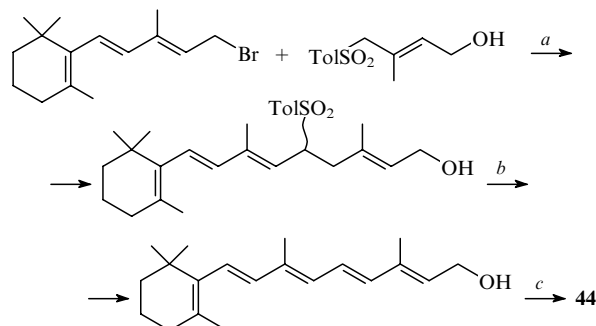
Scheme 4

Path I



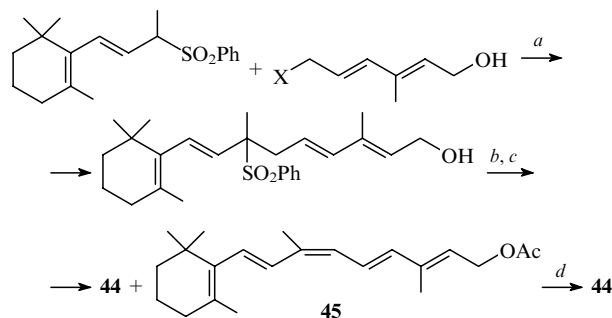
(a) Bu^tOK , THF; (b) Pr^tONa , C_6H_{14} , 30°C , 1 h (82%–86%); (c) EtONa, EtOH, Δ , 13 h (83%), (d) Ac_2O , Py.

Path II

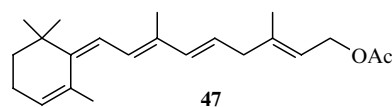


(a) LDA, THF; (b) NaNH_2 , NH_3 (liquid), -30°C , 50 min (85%); (c) Ac_2O , Et_3N .

Path III

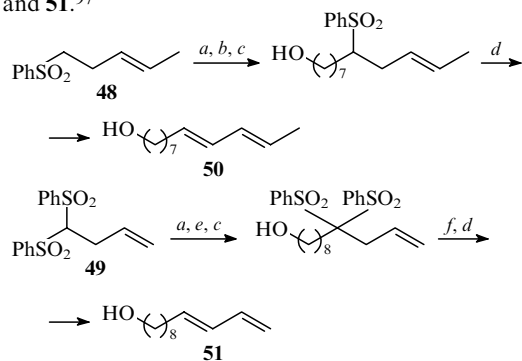


X = Cl, Br; (a) Bu^tOK ; (b) NaOH, Me_2NH , 20°C , 16 h (75%) (ratio **44**:**45** ~ 1:2); (c) AcCl , Py; (d) PdCl_2 (70%).



and II)^{92, 93, 95} and the (C₁₃ + C₇) scheme 4 (path III)⁹⁴ were developed together with several procedures for the elimination of sulfinic acid. The major difficulties were associated with the formation of an admixture of the biologically inactive isomer **45** with the (*Z*)-C(9)=C(10) bond and the isomer **47**. Apparently, the isomer **45** was formed as a result of isomerisation of the intermediate sulfone **46**, whereas the isomer **47** was formed upon prolonged action of a base. The best results were obtained with the use of mild heterogeneous elimination of sulfinic acid (PrⁱONa, hexane, path I *b*). However, isolation of pure retinol acetate (**44**) requires recrystallisation.⁹² Other procedures for elimination (path I *c*, path II *e* and path III *h*) call for a number of additional operations. Thus upon desulfonylation with a solution of NaOH in Me₂NH, the content of the isomer **45** in the reaction mixture reached 34%. After isomerisation under the action of PdCl₂ and recrystallisation, pure retinol acetate was obtained in 70% yield. None of the sulfonyl procedures has been used in industry, at least, before 1984.⁹⁶

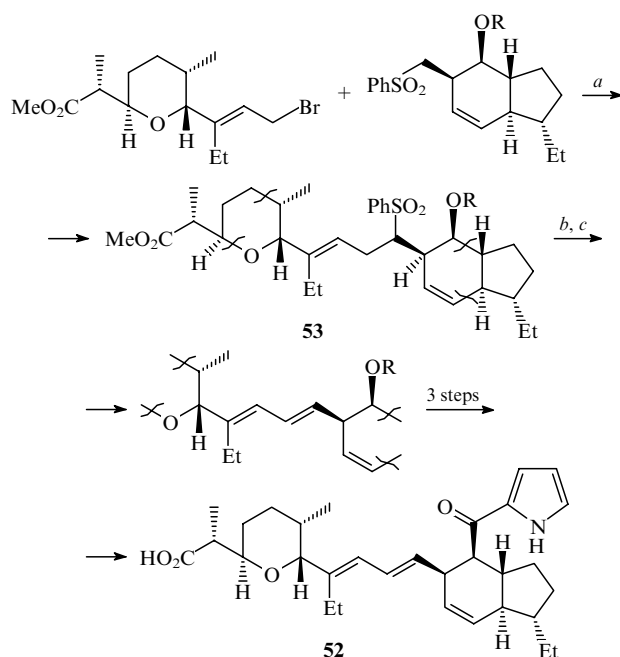
In the case of less complex molecules, for example, in the formation of (*E,E*)-1,3-dienes, the reactions are not accompanied by isomerisation. Therefore, (*E*)-homoallylic sulfones of the types **48** and **49** are convenient starting compounds. Elimination of sulfonic acid was used in the synthesis of pheromone components **50** and **51**.⁹⁷



(a) BuⁿLi; (b) THPO I; (c) H₃O⁺; (d) Bu^tOK, Bu^tOH, Δ;

(e) THPO ~~XX~~ I; (f) Na/Hg.

In the total convergent synthesis of the ionophore antibiotic indanomycin **52**,⁹⁸ the formation of the (*E,E*)-diene bridge

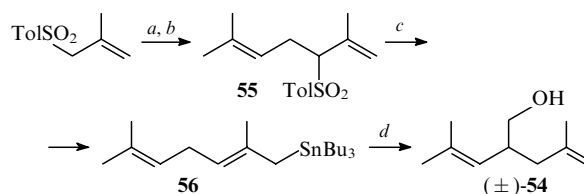


R = SiMe₂Bu^t; (a) LDA, THF, -78 °C (97%);

(b) triton B (BnMe₃NOH), MeOH, 40 °C; (c) CH₂N₂, Et₂O, 0 °C.

between two cyclic fragments of the molecule occurred as elimination of sulfinic acid involving only the hydrogen atom of the acyclic part of the intermediate sulfone **53**.

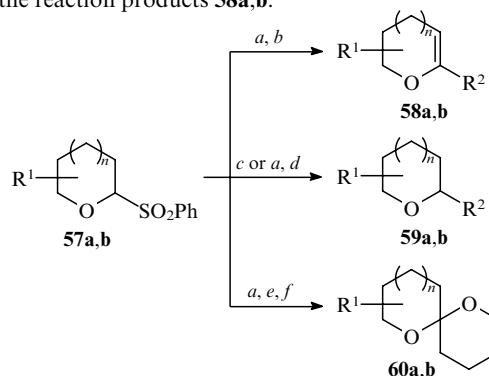
The synthesis of racemic lavandulol ($\pm$)-**54** involved formal replacement of the sulfonyl group.⁹⁹ The intermediate sulfone **55** was hydrostannylated simultaneously with the elimination of sulfinic acid. The subsequent reaction of stannane **56** with trioxane in the presence of boron trifluoride etherate was accompanied by elimination of Bu_3SnH and migration of the double bond.



(a) Bu^nLi ; (b)  (97%); (c) $\text{Bu}_3^{\text{n}}\text{SnH}$, AIBN (azobisisobutyronitrile) (97%); (d) $(\text{CH}_2\text{O})_3$, $\text{Et}_2\text{O} \cdot \text{BF}_3$ (57%).

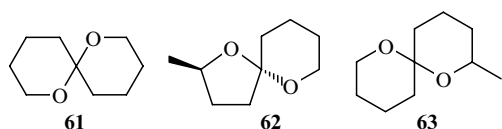
c. Alkylation of α -sulfonyl carbanions with synchronous elimination of sulfinic acid

For saturated molecules, alkylation of α -sulfonyl carbanions with elimination of sulfinic acid is exemplified by the reaction of alkylating reagents with α -carbanions derived from 2-sulfonyl-substituted cyclic ethers, *viz.*, tetrahydropyrans or tetrahydrofurans **57a,b**. The sulfonyl groups in tetrahydropyrans and tetrahydrofurans facilitate α -deprotonation. However, Ley and coworkers¹⁰⁰ found that an intermediate formed in the course of the subsequent reaction with an electrophile is stabilised due to synchronous elimination of sulfinic acid. Apparently, the driving force for this process is the formation of the endocyclic C = C bond in the reaction products **58a,b**.



$n = 0$ (**a**), 1 (**b**); (a) Bu^nLi ; (b) R^2X ; (c) R^2MgX , ZnBr_2 ; (d) R^2X , $\text{C}_{10}\text{H}_8\text{Na}$; (e) $\text{I}(\text{CH}_2)_4\text{OTHP}$; (f) H_3O^+ .

The reactions with Grignard reagents in the presence of zinc salts or with alkyl halides in the presence of sodium naphthalenide afforded tetrahydro derivatives **59a,b**, which are the formal replacement products of the sulfonyl group, instead of dihydropyrans or dihydrofurans **58a,b**. The reactions of the sulfones **57** with electrophiles containing a protected hydroxy group at the ω -position are of considerable interest for the synthesis of certain natural compounds. These reactions afford spiroketals **60** because the hydroxy group of the substituent in the intermediate **58** immediately reacts with the nucleophilic double bond after deprotection in an acidic medium. The simplest examples of this approach are the syntheses of 1,7-dioxaspiro[5.5]undecane (**61**), which is a component of the pheromone of *Dacus Olea*¹⁰¹ and of the so-called fruit flies particularly widespread in tropical countries,¹⁰² as well as the syntheses of analogous compounds **62** and **63**.¹⁰¹



synthesis, was obtained.

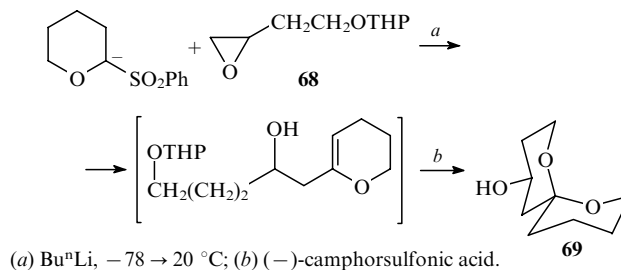
Chemical reaction scheme showing the synthesis of compound **64** from compound **65** and a substituted tetrahydropyran derivative.

Reaction 1: Compound **65** (a 1,3-dioxane derivative with a PhSO_2 group and an OBn group) reacts with a substituted tetrahydropyran derivative (a 2,2-dimethyl-4-iodo-2,3-dihydro-4H-pyran derivative) to form an intermediate.

Reaction 2: The intermediate reacts with compound **66** (a 1,3-dioxane derivative with a PhSO_2 group and an $\text{OSiPh}_2\text{Bu}^t$ group) and another substituted tetrahydropyran derivative (a 2,2-dimethyl-4-iodo-2,3-dihydro-4H-pyran derivative) to form compound **67**.

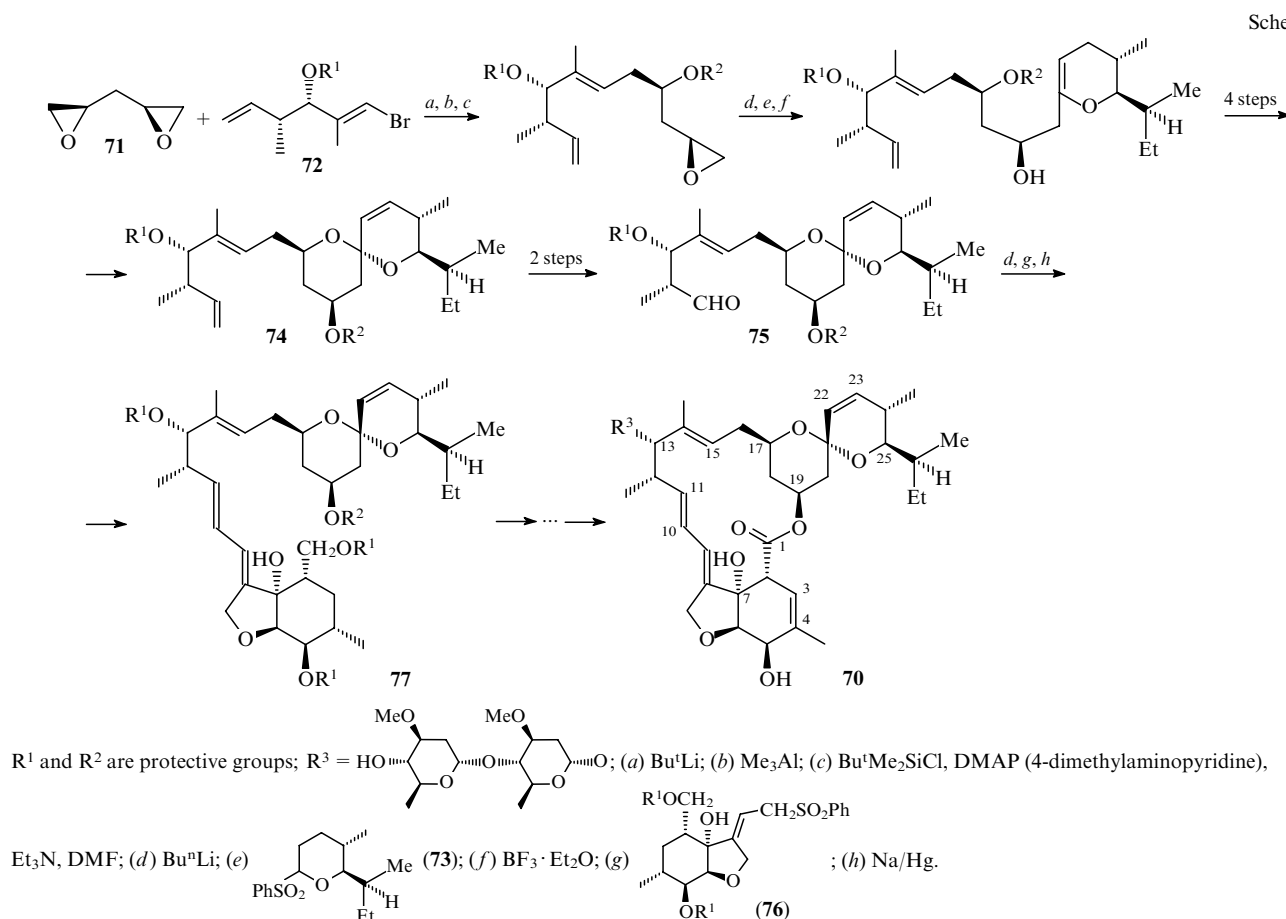
Reaction 3: Compound **67** (a 1,3-dioxane derivative with a PhSO_2 group and a $(\text{CH}_2)_2\text{OH}$ group) is converted to compound **64** (a complex molecule containing a 1,3-dioxane derivative, a 1,3-dioxolane derivative, and a 1,3-dioxane derivative with a PhSO_2 group and a $(\text{CH}_2)_2\text{OH}$ group).

Ley and coworkers started their studies in this field with the development of a procedure for the synthesis of substituted spiroketals by reactions of anions generated from 2-sulfonyl-tetrahydropyrans with new reagents, *viz.*, alkoxy-substituted epoxides of the type **68**. For example, this procedure was used for the synthesis of a minor component (**69**) of the pheromone of olive moth.¹⁰⁵



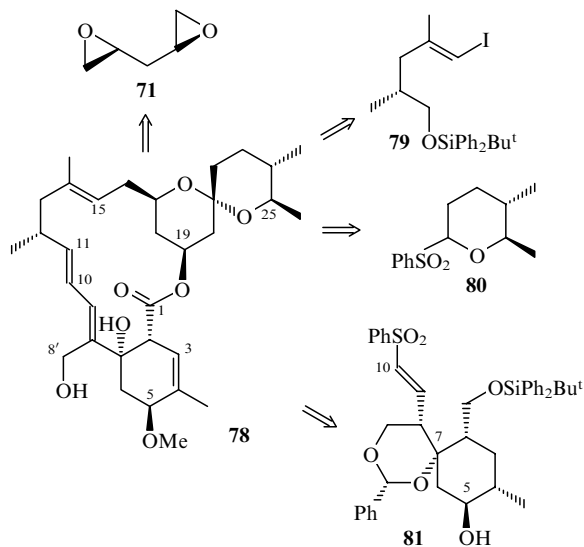
The key steps of the total synthesis of avermectin (**70**) containing 30 stereogenic centres, five C=C bonds with a fixed configuration and numerous functional groups are given in Scheme 5. In particular stages of the synthesis, the intermediates were compared with the degradation products of natural avermectin. The first step of the synthesis of the macrolide **70** involved

† Avermectin was isolated from actinomycete MA-46650 in 1978.¹⁰⁴



the reaction of enantiomerically pure diepoxide **71** [an important synthon for the C(17)–C(19) fragment] with a vinylic bromide **72** to form a substituted epoxide. Subsequent reactions with substituted 2-sulfonyltetrahydropyran **73** followed by transformations required for the formation of the C(22)=C(23) bond afforded spiroketal **74**, which is the ‘northern’ [C(11)–C(25)] hemispherical fragment of the macrolide **70**. The terminal C=C bond in the compound **74** was converted into the aldehyde group in two steps. The reaction of the intermediate **75** with the anion generated from allylsulfonyl synthon **76** resulted in the formation of the (*E*)-C(10)=C(11) bond (the Julia olefination, Section III.2.a). Compound **77** contained ~12% of an admixture of the (*Z*)-C(10)=C(11) isomer. The completion of the synthesis involved the macrolactonisation of the intermediate **77** following oxidation at C(1) with simultaneous formation of the C(3)=C(4) bond and the attachment of the disaccharide residue R³, which was obtained from oleandrose, at C(13).

The synthesis of a somewhat less complex molecule, *viz.*, melbemycin β₁ (**78**), was carried out according to an analogous scheme.¹⁰⁷ The major synthons in this scheme are either identical to compounds used for the preparation of avermectin (**70**) (for example, diepoxide **71**) or differ only in the functional groups (synthons **79**, **80** and **81** correspond to compounds **72**, **73** and **76**, respectively). The formation of spiroketal is also a fundamental step in the construction of the ‘northern’ fragment. The coupling of the ‘northern’ and ‘southern’ fragments to form the (*E*)-C(10)=C(11) bond was performed by the reaction of the aldehyde group of the ‘northern’ fragment with the α-sulfonyl carbanion of the ‘southern’ fragment. This reaction is not the standard olefination procedure according to Julia because the C(9)=C(10) double bond is converted into the required C(10)=C(11) bond.¹⁰⁷



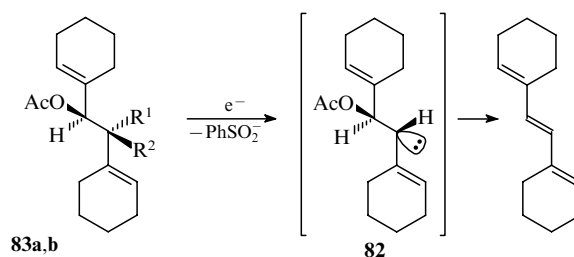
The common feature in the syntheses of the macrolides **70** and **78** is the method of formation of the trisubstituted C(14)=C(15) bond. This bond is introduced upon reactions with the halide synthons **72** or **79**. This makes it possible to circumvent the difficulties encountered in earlier studies (see Section III.2.a) in attempting to construct this bond with the use of sulfonyl or sulfenyl precursors.

2. Addition to oxygen-containing electrophiles

a. Addition of α-sulfonyl carbanions to carbonyl groups of aldehydes and ketones

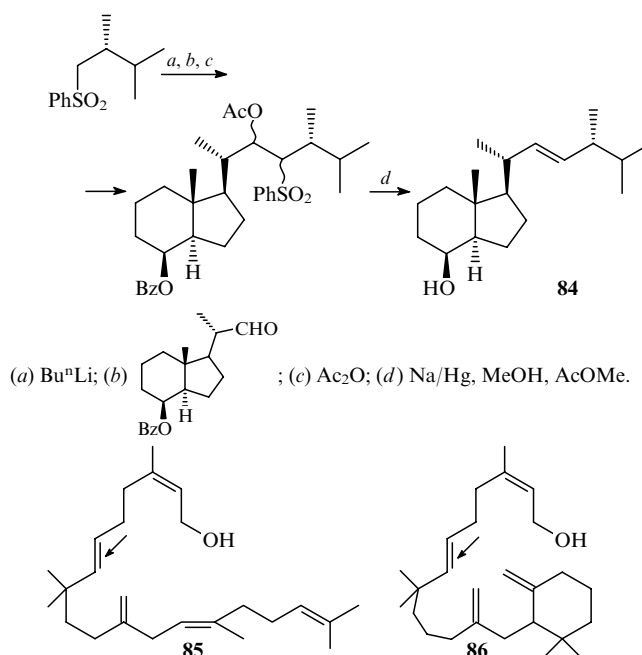
Lythgoe¹⁰⁸ and Kocienski^{109–111} have shown that an important problem of olefination (coupling of synthons with the stereospecific formation of the C=C bond) can be solved by reductive elimination of 2-hydroxy sulfones, which are prepared by the reactions of aldehydes with α-sulfonyl carbanions, proposed by

Julia and Paris.³⁶ This procedure is an excellent alternative to the phosphonate Wittig method. The optimum conditions for olefination were found, *viz.*, acetylation or benzylation of the hydroxy group and reductive elimination with sodium amalgam in a mixture of methanol with tetrahydrofuran or ethyl acetate.¹¹² In studies of the scope and limitations of this reaction, it was demonstrated that *E*-disubstituted double bonds can be formed with a stereoselectivity of ~80%–100%. The stereoselectivity is enhanced in the case of chain branching at the β-position with respect to the double bond, whereas a substituent at the α-position hinders the reaction.¹¹³ Trisubstituted C=C bonds are formed with difficulty and the stereoselectivity of this process is low, whereas attempts to obtain tetrasubstituted C=C bonds failed.¹⁰⁹ Since the stereochemistry of the initial acyloxy sulfone (*threo*-, *erythro*- or a mixture of both forms) has no effect on the stereoselectivity of the formation of the C=C bond, it was suggested that this process occurs *via* a common intermediate **82** formed upon reductive elimination of the sulfinate anion or from the diastereomers **83a** or **83b**.^{109, 113} The intermediate **82** is long-lived enough to assume the conformation favourable for elimination of the acyloxy anion. This may not be the case with ketones exerting steric hindrances, which explains the fact that olefination with the use of acyloxysulfonyl derivatives prepared from ketones is not always successful. Recently, a more intricate mechanism of the olefination has been proposed.¹¹⁴ However, none of the suggested reaction schemes was confirmed by quantitative methods, for example, by kinetic methods.



R¹ = H, R² = SO₂Ph (**a**); R¹ = SO₂Ph, R² = H (**b**).

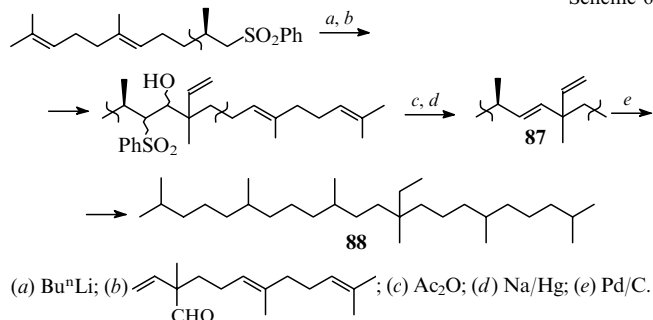
Below are summarised the results of the use of this methodology in the syntheses of natural compounds performed by Kocienski and Lythgoe with their coworkers. This procedure was used for the formation of the (*E*)-C=C bond in the alcohol **84**, which is the key intermediate in the synthesis of calciferol,¹¹⁵ and for the preparation of different modifications of vitamin D,



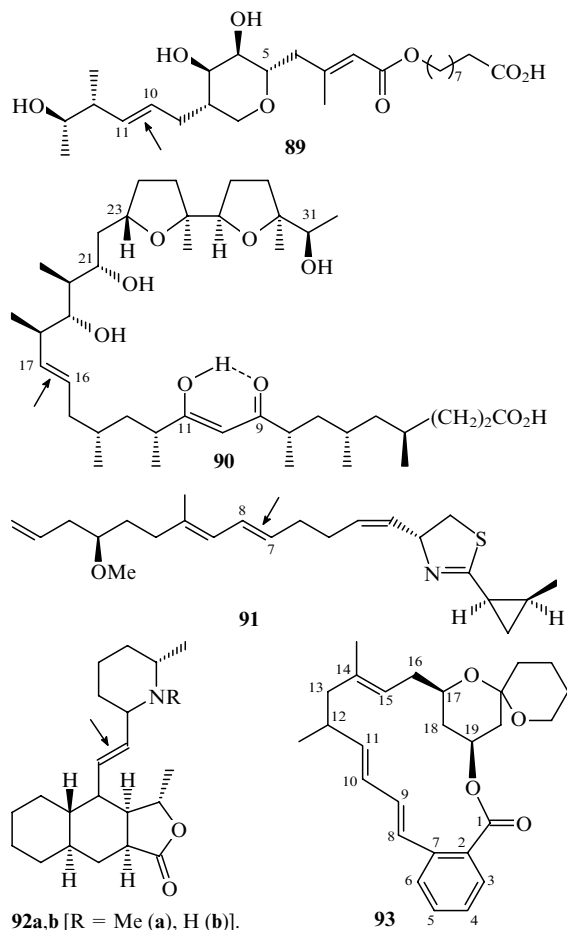
including α -hydroxy vitamin D₃ (see Ref. 116) and vitamin D₄.¹¹⁷ (More recently,¹¹⁸ 25-hydroxy vitamin D₂ was prepared according to an analogous procedure with the use of ethylmagnesium bromide instead of BuLi for deprotonation). This scheme was applied to the synthesis of the major C₂₅ segments (**85** and **86**) for the preparation of the antibiotics moenocinol¹¹⁹ and diumycinol,¹²⁰ respectively.

Later, the Julia olefination (which is sometimes called the Julia–Kocienski or the Julia–Lythgoe olefination) has found wide application in the synthesis. Thus this procedure was used in the synthesis of botryococcene **87** (Scheme 6), which is an algae hydrocarbon. The compound **87** has a specific branched structure. The product of its exhaustive hydrogenation (**88**) is a promising biological marker in petroleum production.¹²¹

Scheme 6



Olefination is the major stage in the total syntheses of a number of biologically active long-chain compounds. This reaction has been used in the formation of the (*E*)-C(10)=C(11) bond in the antibiotic pseudomonic acid C (**89**),^{122,123} the C(16)=C(17) bond in the antibiotic ionomycin (**90**) responsible for the transport of Ca²⁺ ions^{124,125} and the C(7)=C(8) bond in the diene fragment of curacin (**91**) exhibiting antitumor activity.¹²⁶ To construct the double bond between the piperidine and decahydronaphthalene fragments in the synthesis of alkaloids (+)-himbacine (**92a**) and (+)-himbeline (**92b**), the aldehyde and sulfonyl groups should be bound to the pyrimidine and decahydronaphthalene synthons, respectively,¹²⁷ otherwise steric hindrance to olefination occurs. One of the double bonds of the 1,3-diene system of indanomycin was also formed according to this procedure.¹²⁸



The Julia olefination is often used for the introduction of C=C bonds into the starting compounds which are subsequently employed in total syntheses. For example, double bonds in the following fragments were formed according to this procedure: in the C(1)–C(22) fragment for the construction of immunodepressant FK,¹²⁹ in the C(22)–C(31) fragment of an intermediate for the macrolide antibiotic roxatidin¹³⁰ and in the triene group of the C(10)–C(27) fragment used in the synthesis of the immunodepressant rapamycin.^{131,132} In the total synthesis of the antitumor macrolide aplyronine, coupling by the reaction of the α -sulfonyl anion with the aldehyde group was employed twice.¹³³ When the C(3)–C(17) fragment was constructed in the synthesis of boromycin, the intermediate 2-hydroxysulfonyl unit was used for the stereoselective formation of the hydroxy group rather than for the introduction of the double bond.¹³⁴

The Julia olefination was also used in the total syntheses of the majority of macrolides of the avermectin — melbemycin group, for example, of avermectin B1a (Ley *et al.*,¹⁰⁶ Hanessian *et al.*¹³⁵ and White *et al.*¹³⁶), as well as of the simplest compound of this group, *viz.*, melbemycin β_3 (**93**), which served as the favourite subject in earlier synthetic studies performed by Kocienski,¹³⁷ Baker¹³⁸ and Barrett¹³⁹ with their coworkers.

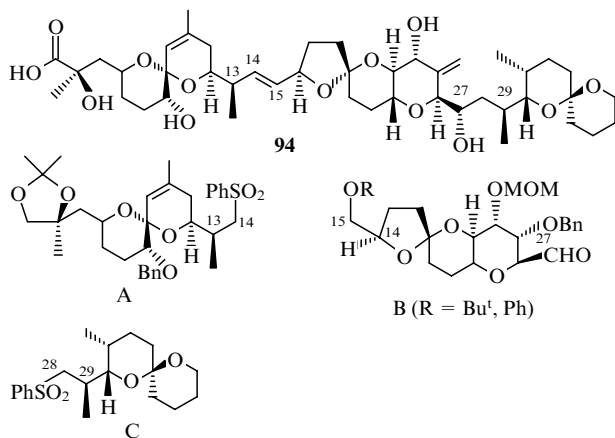
The Julia procedure was used for the coupling of large fragments which have been synthesised beforehand and already contained the required chiral centres. Macrolactonisation was performed in the final stage of the synthesis. In the synthesis of these very complex systems, the previously established regularities hold on the whole. The formation of the disubstituted C(10)=C(11) bond occurs most readily and with a high stereoselectivity, particularly, when the aldehyde group is bound to the C(11) atom of the 'northern' fragment, while the sulfonyl group is bound to the C(10) atom of the 'southern' fragment.^{106,137} When the functional groups are located in the reverse order, the results are somewhat worse.^{135,138} When the ketone was used in place of the aldehyde for the formation of the C(8)=C(9) bond of avermectin B1a [the carbonyl group at the C(8) atom of the 'southern' fragment and the sulfonyl group at the C(9) atom of the 'northern' fragment],¹³⁶ the reaction was complicated by lactonisation of the intermediate. The formation of the trisubstituted C(14)=C(15) bond with the use both of the ketone¹³⁶ and aldehyde¹³⁹ versions of olefination occurs in low yield and affords an admixture of an undesirable regioisomer. With the aim of constructing this bond, more sophisticated approaches, though also based on reactions of sulfoxides and sulfones, were applied.^{136,139}

Kocienski was the first to note¹⁰⁹ that the use of olefination for the preparation of large amounts of compounds is hampered by the necessity of consuming a considerable amount of amalgam for desulfonation. Presently, a number of procedures free of this drawback are available. Thus it is believed¹⁴⁰ that reduction with magnesium in ethanol upon catalysis with mercuric chloride occurs due to *in situ* formation of magnesium amalgam. It was also recommended to use SmI₂ in THF¹⁴¹ or HMPA.^{141,142} In the latter case, a trisubstituted double bond is successfully formed from ketones and primary sulfones, though only in low-molecular-weight model compounds.

Reactions of α -sulfonyl anions with aldehyde groups have also been used for the coupling of bulky, *e.g.*, cycloaliphatic, segments. This coupling not necessarily involved the formation of the C=C bond, but sometimes occurs through hydroxy- or oxo-functionalised saturated units.

The key steps in a multistep (more than 100 steps) enantio- and stereospecific total synthesis of okadaic acid **94**, which is a

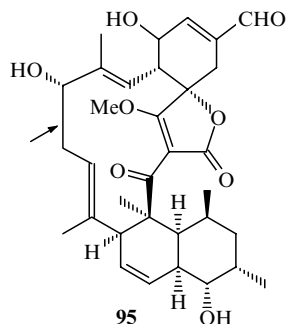
potential antitumor drug,[‡] involved couplings of the segments A, B and C, which have been prepared according to the retrosynthetic approach, in the order (B + C) + A (the atomic numbering scheme corresponds to that used for okadaic acid).^{144–147}



MOM is methoxymethyl.

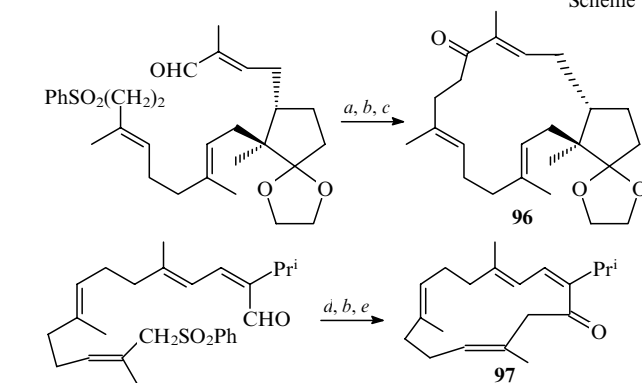
D-Glucose derivatives served as chiral pools for the construction of the segments A, B and C. The OH group at C(27) was obtained by transformation of the 2-hydroxysulfonyl grouping formed by the reaction of the aldehyde group of the segment B with the anion from the sulfone C, and the C(14)=C(15) double bond was formed according to Julia with the participation of the sulfonyl centre of the segment A. The stereoselective introduction of the methyl groups at C(13) in the segment A¹⁴⁵ and at C(29) in the segment C¹⁴⁷ was performed according to 'heteroconjugate addition' to α -silyl vinyl sulfones developed by Isobe and co-workers (this procedure will be considered in more detail in Section V.1). The final steps in the total synthesis of acid **94** with the construction of all its 17 chiral centres involve deprotection of the functional groups and conversion of 1,2-acetonide into the hydroxy acid.

The use of intramolecular reactions of α -sulfonyl carbanions with aldehydes^{148–151} is exemplified by the synthesis of tetronolide **95**, which is the aglycone of the antitumor antibiotic tetrocarcin,^{148, 149} as well as by the construction of a bicyclo-[13.3.0]octadecane core **96** for the synthesis of terpestacin and of a 14-membered core **97** for the preparation of sarcophytol A.¹⁵⁰ Syntheses of the compounds **96** and **97** involved oxidation of hydroxy groups to carbonyl groups followed by reductive removal of the sulfonyl group (Scheme 7), while the synthesis of the compound **95** additionally involved stereospecific reduction of the carbonyl group to the hydroxy group. Attempts to use this approach in the synthesis of the antitumour antibiotic lankacidin were unsuccessful. Apparently, this is associated with the use of the imidazolesulfonyl group.¹⁵²



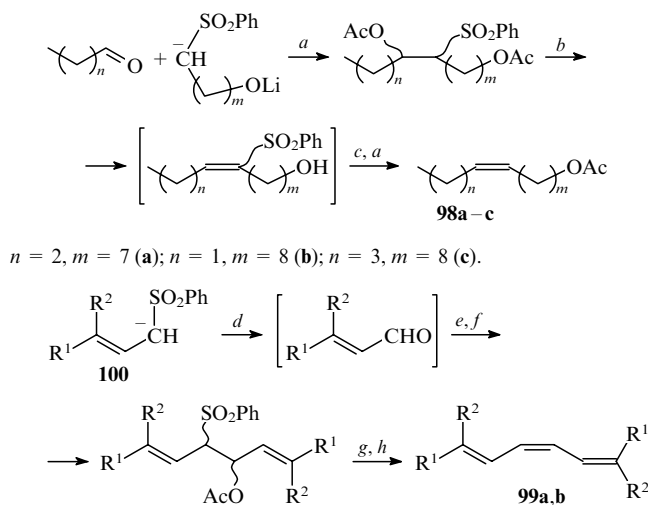
[‡] It was believed¹⁴³ that acid **94** and its esters isolated from marine algae are toxins, which cause mortality of the gastroenteritis type as a result of diarrhetic shellfish poisoning.

Scheme 7



(a) LiHMDS, PhH, 25 °C; (b) oxidation; (c) Al/Hg; (d) LiHMDS, PhH, 22 °C, 5 min; (e) SmI₂, THF.

The Z-olefination method, which has also been developed by Julia,³⁷ is applied more rarely than the E-version. In this case, a mixture of diastereomeric acyloxy sulfones generated originally was treated with a strong base followed by desulfonylation of an intermediate (Z)-vinyl sulfone to form (Z)-alkene. This procedure was used for the preparation of components of the pheromones **98a–c** [98% of the (Z)-isomers],³⁷ dehydro-(Z)-12-squalene (**99a**) and (Z)-16-phytoene (**99b**) (in both cases, the selectivity was ~ 87%).¹⁵³ In the latter case, the aldehyde component was generated *in situ* by oxidation of a portion of the α -sulfonyl carbanions **100**.

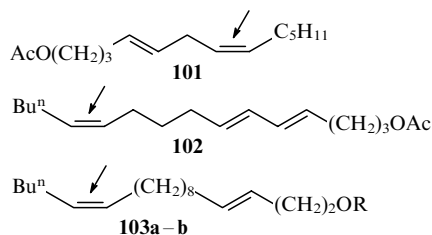


99a: R¹ = $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CHCH}_2$, R² = Me;

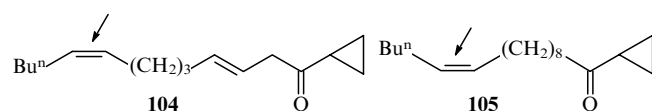
99b: R¹ = $\text{CH}_3(\text{CH}_2)_5\text{CH}=\text{CHCH}_2$, R² = Me;

(a) Ac₂O; (b) NaOH; (c) Na₂S₄O₆; (d) MoO₅, Py, HMPT; (e) **100**; (f) Ac₂O, Et₃N; (g) NaH, THF; (h) BuⁿMgX, Ni(acac)₂.

Later on, Moiseenkova and Nefedov with coworkers^{154–156} slightly improved the procedure for Z-olefination and applied it to the synthesis of trideca-(4E),(7Z)-dien-1-yl acetate (**101**) (the potato moth pheromone)¹⁵⁵ and (E,Z)- and (E,E,Z)-acetogenin

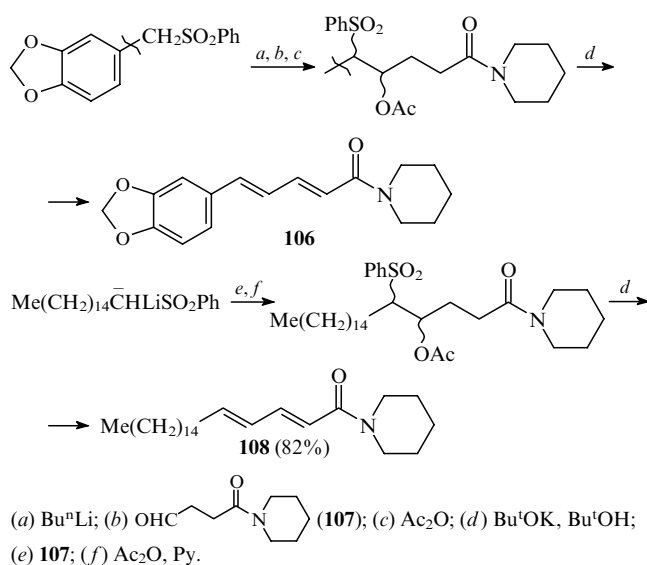


R = Ac (**a**), H (**b**).

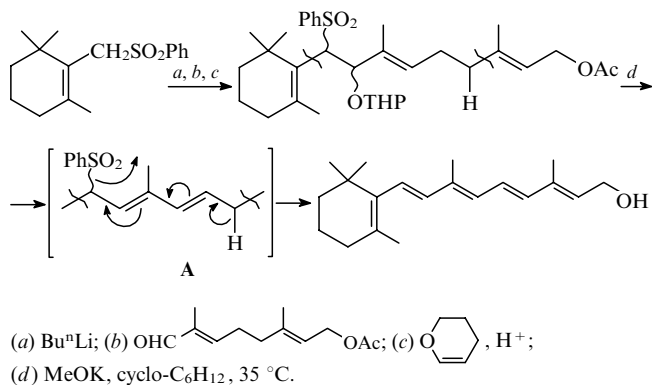


pheromones **102** and **103a,b**.¹⁵⁵ The previously unknown cyclopropane ketones **104** and **105** served as the key compounds in the syntheses of the latter compounds (in the schemes, the double bonds formed with the use of the α -sulfonyl carbanions are indicated by arrows).

Otera and coworkers^{157–160} elaborated a procedure for the transformation of ethers of 2-hydroxy sulfones through double elimination. This procedure extends the possibilities of application of reactions of sulfonyl carbanions with aldehydes. Initially, acyloxy or alkoxy groups in esters and ethers of 2-hydroxy sulfones are eliminated under the action of a strong base (generally, Bu^tOK) followed by dehydrosulfinylation of vinyl sulfone to form the acetylene bond. If allylic isomerisation can occur in the stage of generation of unsaturated sulfone, an *E,E*-diene system is formed. The latter procedure has been used¹⁵⁹ for the preparation of piperine **106**, which is one of the components of black pepper, starting from the aldehyde **107**. Yet another natural dienamide, viz., trichonine (**108**), was also prepared according to this procedure [85%, 10% and 5% of the (2*E*,4*E*)-, (2*E*,4*Z*)- and (2*Z*,4*E*)-isomers, respectively].¹⁶⁰



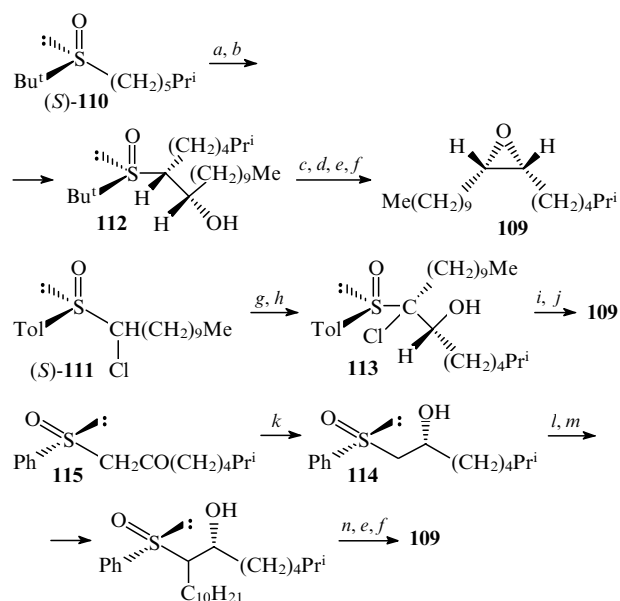
An ingenious convergent (C₁₀ + C₁₀) scheme for the synthesis of vitamin A was also developed.^{161,162} Tetrahydropyran-2-yl ethers of 2-hydroxy sulfones proved to be the starting compounds of choice for this sequence of reactions. In the first step, the second allylic bond was established with respect to the sulfonyl group. Elimination of sulfinic acid from the intermediate **A** occurred with the participation of the remote allylic hydrogen atom at C(12). The resulting vitamin A contained > 85% of the all-*trans* isomer;



this amount is substantially greater than those obtained with the use of other sulfonyl methods (see Section III.1.b).

b. Addition of α -sulfinyl carbanions to carbonyl groups of aldehydes and ketones

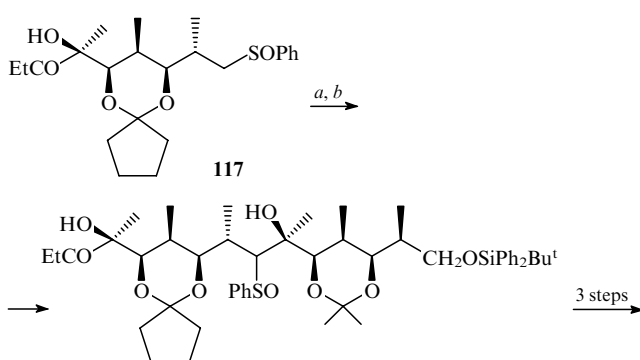
As mentioned above (Section II), epimeric mixtures of 2-hydroxy sulfoxides formed in the reactions of aldehydes with α -sulfinyl carbanions are rather rarely used in the synthesis of natural products. The synthesis of the enantiomerically pure pheromone (+)-(7*R*,8*S*)-disparlure (**109**) by the reaction of the corresponding aldehydes with enantiomerically pure (*S*)-*tert*-butyl 6-methylheptyl sulfoxide (**110**)¹⁶³ or (*S*)- α -chlorododecyl tolyl sulfoxide (**111**) is one of a few examples.¹⁶⁴

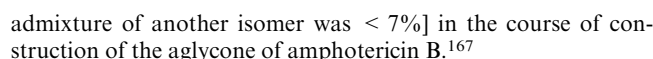


(a) Bu^tLi; (b) Me(CH₂)₉CHO (45%); (c) SnCl₂, AcCl; (d) LiAlH₄; (e) Me₃OBu^t; (f) NaOH; (g) LDA; (h) Prⁱ(CH₂)₄CHO (39%); (i) Bu^tOK, Bu^tOH; (j) BuⁿLi, THF, -100 °C; (k) Bu₂AlH; (l) MeLi; (m) C₁₀H₂₁I; (n) Zn, Me₃SiCl.

The total yield of the compound **109** was low because hydroxy sulfoxides **112** and **113** were obtained as mixtures of diastereomers. The procedure with the use of enantiomerically pure 2-hydroxy sulfoxide **114**, which is prepared by stereoselective reduction of oxo sulfoxide **115**, is approximately twice as efficient.¹⁶⁵

The ratio of the diastereomers in a mixture of 2-hydroxy sulfoxides depends on the nature of substituents in the initial sulfoxide and aldehyde. Stork and coworkers¹⁶⁶ reported that the reaction of sulfoxide **117** with ketone **118**, which was used in a rather simple synthesis of protected chiral polyol **116** containing all 10 asymmetric centres of the secoacid of the aglycone of erythromycin, afforded a mixture of 2-hydroxy sulfoxides containing 80% of the target epimer. Compound **119** was obtained [the C(1)–C(12) fragment with the required configuration; the



[illegible]

The stereo- and enantioselectivity of the reactions of α -sulfinyl carbanions with aldehydes increases in the presence of alkoxy-carbonyl groups adjacent to the carbanionic centre.¹² This can be demonstrated by syntheses of enantiomerically pure pheromone lactams¹⁶⁹ and maytansin¹⁷⁰ exhibiting antitumour activity.

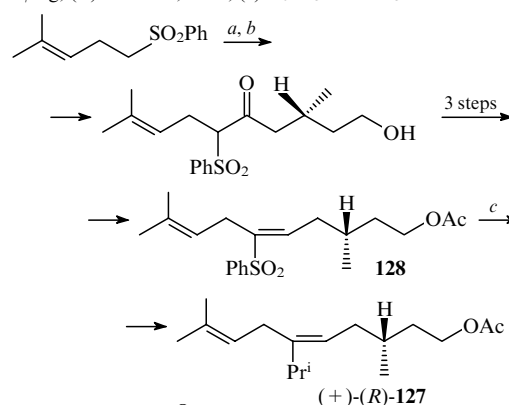
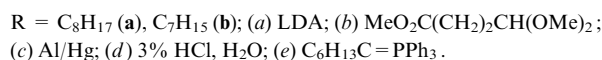
O=C1C(=O)C(=O)C(=O)C(=O)C(=O)C(=O)C(=O)C1

O (-)-123

$$\begin{array}{c} \text{R}^1\text{S}(\text{O})\text{CH}_2\text{Z} + \text{R}^2\text{R}^3\text{CHCHO} \xrightarrow{a} \left[\begin{array}{c} \text{R}^2\text{R}^3\text{CHCH}=\text{C}(\text{Z})\text{SR}^1 \\ \text{A} \quad \quad \quad \text{O} \end{array} \right] \rightarrow \\ \rightarrow \begin{array}{c} \text{R}^2\text{R}^3\text{C}=\text{CHCH}(\text{Z})\text{SR}^1 \\ \text{B} \quad \quad \quad \text{O} \end{array} \rightarrow \begin{array}{c} \text{R}^2\text{R}^3\text{CCH}=\text{CHZ} \\ \text{OSR}^1 \quad \quad \text{C} \end{array} \right] \rightarrow \\ \rightarrow \text{R}^2\text{R}^3\text{C}(\text{OH})\text{CH}=\text{CHZ} \\ \text{D} \end{array}$$

Since α -sulfinyl-substituted carbonyl compounds are most commonly used as the starting materials in this reaction, the latter is abbreviated to SPAC (Sulfoxide Piperidine and Carbonyl).

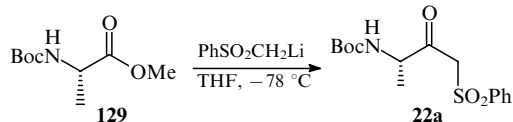
In the absence of such competition, the reactions involving ester groups, including lactone groupings, proceed readily. Reactions of α -sulfonyl carbanions with esters were used for the construction of the intermediates **124a,b** in the syntheses of components of pheromones of peach moth, *viz.*, of (*Z*)-eicos-13-en-10-one (**125a**) and (*Z*)-nonadec-12-en-9-one (**125b**).¹⁷⁷ Julia and coworkers¹⁷⁸ prepared the pheromone of yellow scale (**127**) starting from enantiomerically pure lactone (*R*)-**126**. In this synthesis, advantages were taken of yet another interesting reaction, which has been discovered in the same laboratory,⁴¹ *viz.*, the replacement of the sulfonyl group in the intermediate **128** under the action of isopropylmagnesium chloride in the presence of FeCl_3 .



(a) BuⁿLi; (b)  O[(*R*)-**126**]; (c) PrⁱMgCl, FeCl₃.

The reaction of the sulfonyl anion with the ester group served as the key step¹⁷⁹ in the stereocontrolled synthesis of pseudoan-nonacin A.

The oxo sulfone **22a**, which is the reaction product of lithiated methyl phenyl sulfoxide with protected alanine methyl ester **129**,¹⁸⁰ was used in the synthesis of isosteres of peptides.⁸⁰



The reaction of α -sulfonyl anions with esters was used as the key step in the construction of the macrolide brefeldin A (**130**) (which is related to prostaglandin and is a highly active fungicidal and antitumour drug,^{181, 182}) and of the corresponding secoacid **131**.¹⁸³

The compound **130** was prepared both in racemic and optically active forms, whereas the acid **131** was obtained only in the optically active form. In all three cases, the lower branch was constructed *via* substituted oxo sulfones **132**–**134** using similar procedures (Scheme 8).

The phosphonate method was used for the construction of the (*E*)-C(10)=C(11) bond in brefeldin (**130**),^{181, 182} while Trost *et al.*¹⁸³ made use of the Julia methodology to form this bond in compound **131** following reduction of the oxo group in the intermediate **134** to the hydroxy group. The C(2)=C(3) bond and the chiral centre at C(4) were generated with the use of various procedures for the introduction of the sulfinyl group^{181, 183} followed by thermolysis. This methodology is described in more detail in Section IV.

The intramolecular reactions under consideration have also been used for the synthesis of polycyclic terpenoids, for example, trinoranastreptene¹⁸⁵ or precursors for guaiane terpenoids.^{186, 187} A general procedure for the synthesis of terpenoids with fused

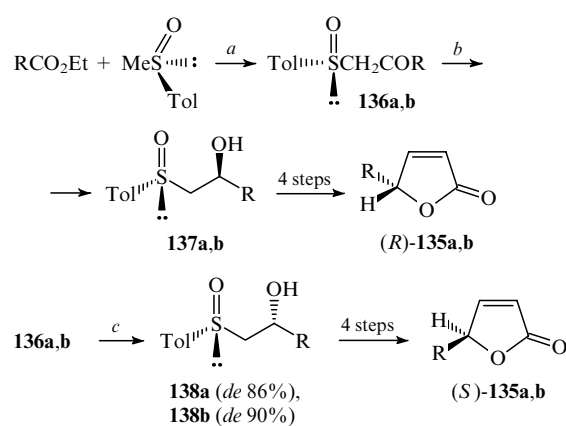
medium-sized rings involving intramolecular reactions of α -sulfonyl carbanions with esters was also proposed.¹⁸⁸

d. Reactions of α -sulfinyl carbanions with esters

Owing to the development of enantioselective procedures for the reduction of oxo sulfoxides,^{12, 27} which can be readily prepared by reactions of α -sulfinyl carbanions with esters, enantiomerically pure chiral 2-hydroxy sulfoxides became readily accessible compounds and found wide use in asymmetric synthesis, including the preparation of biologically active compounds.¹²

Thus 4-substituted butenolides **135a,b** both with the *R*- and *S*-configurations of the asymmetric centre were prepared from the same oxo sulfoxide **136a** or **136b**.¹⁸⁹

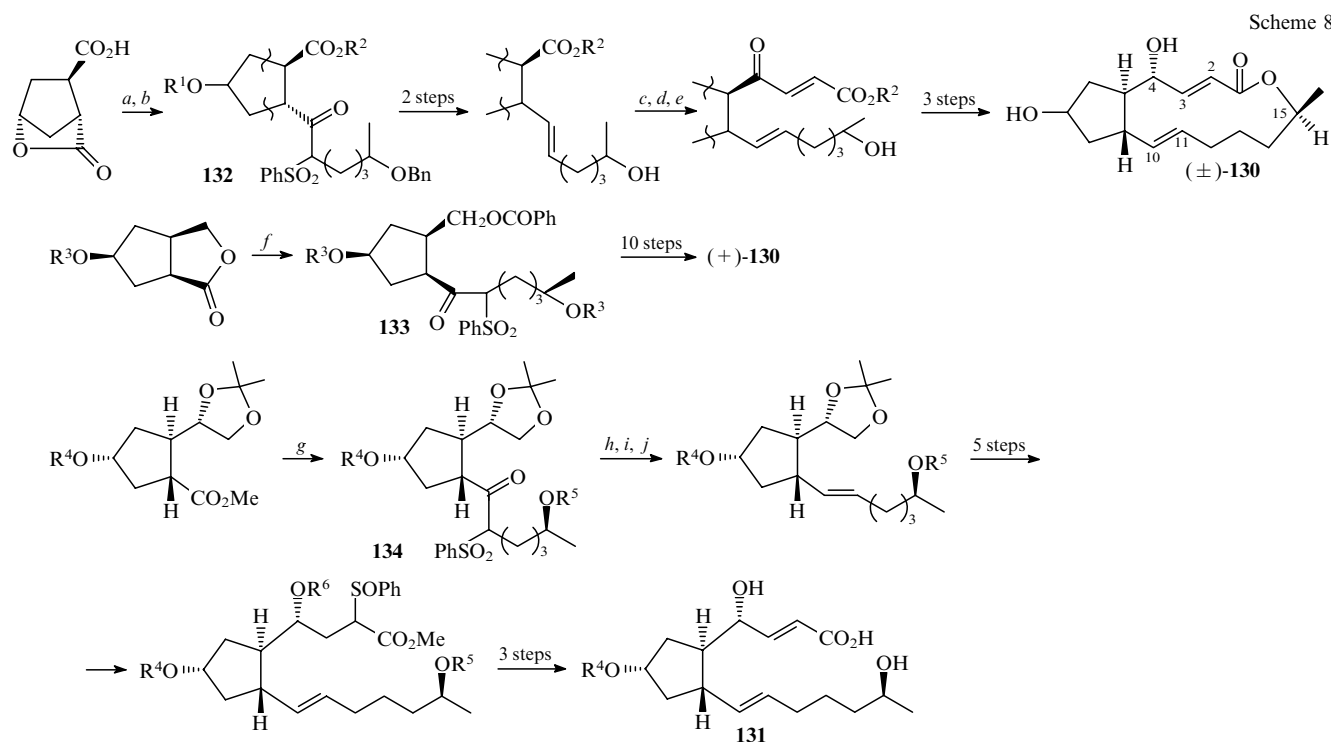
The high enantioselectivity in the synthesis of 2-hydroxy sulfoxides **137a,b**, which are required for the preparation of *R*-enantiomers of butenolides **135a,b**, was achieved by the addition of ZnCl_2 in the course of hydride reduction of the oxo sulfoxides **136a,b**. In this case, a rigid chelate complex of zinc



$\text{R} = \text{Bu}^t$ (**a**), C_8H_{17} (**b**); (a) LDA; (b) Bu_2AlH , ZnCl_2 ; (c) Bu_2AlH .

involving both functional groups of the oxo sulfoxide was formed as a result of which the hydride attack occurred from the required side. Reduction of the oxo sulfoxides **136a,b** without addition of

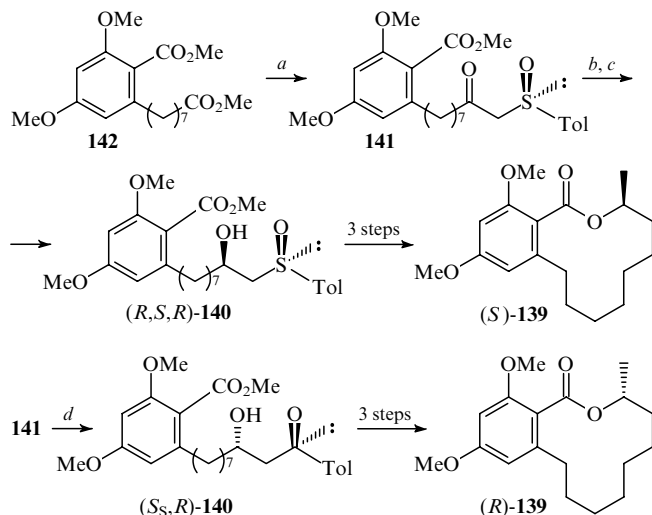
§An analogous procedure was used for the construction of the lower branch in more recent syntheses of brefeldin.¹⁸⁴



R^1 – R^5 are protective groups; (a) $\text{PhSO}_2\text{CH}(\text{CH}_2)_3\text{CH}(\text{OBn})\text{Me}$; (b) R^2Cl , EtPr_2N ; (c) Me_2SO , NaOH ; (d) $\text{BrCH}_2\text{CO}_2\text{Me}$; (e) Δ ; (f) $\text{PhSO}_2\text{CH}(\text{CH}_2)_3\text{CH}(\text{OR}^3)\text{Me}$; (g) $\text{PhSO}_2\text{CH}(\text{CH}_2)_3\text{CH}(\text{OR}^5)\text{Me}$ (90%–96%); (h) NaBH_4 ; (i) Ac_2O ; (j) Na/Hg , Na_2HPO_4 (65%).

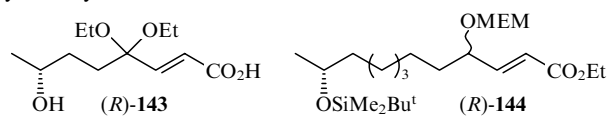
ZnCl₂ afforded hydroxy sulfones **138a,b** with a high diastereoselectivity. The latter were transformed into the *S*-enantiomers of the butenolides **135a,b**.

An analogous approach was used in the synthesis of macrocyclic diethers for the preparation of enantiomerically pure diethers of lasiodiplodins, (*R*)- and (*S*)-**139**.¹⁹⁰ Epimeric 2-hydroxy sulfoxides **140** were synthesised by the reduction of oxo sulfoxide **141** in the presence or in the absence of ZnCl₂. It should be noted that when the compound **141** was prepared from diester **142** and the chiral sulfinyl anion, only the methoxycarbonyl group of the aliphatic chain was involved in the reaction, while the methoxycarbonyl group in the aromatic ring remained intact and was subsequently used for the construction of the macrocyclic lactone fragment.

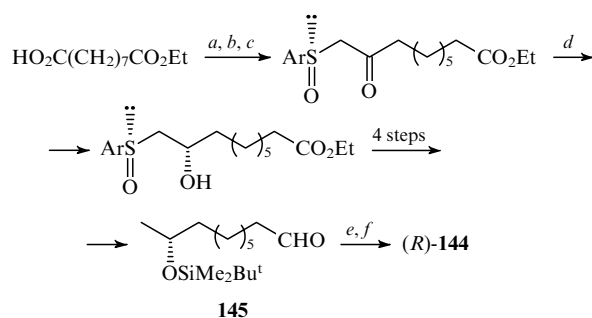


(a) 2.2 equiv. of $\text{LiCH}_2\text{S(O)Tol}$, THF, -78°C ; (b) ZnCl₂; (c) Bu_2AlH , 20°C (*de* > 95%); (d) Bu_2AlH , THF, -78°C , (*de* 86%).

Chiral sulfinyl groups of 2-hydroxy sulfoxides served as inductors in diastereospecific syntheses of the protected secoacids **143** and **144** representing degradation products of the macrocyclic diethers (*R,R*)-pyrenophorin and (*R*)-patulolide A, respectively.¹⁹¹ The γ -hydroxy- α,β -unsaturated fragment of the secoacid **144** was constructed by the SPAC-type reaction of aldehyde **145** with the ethyl sulfinylacetate anion.^{172–174}

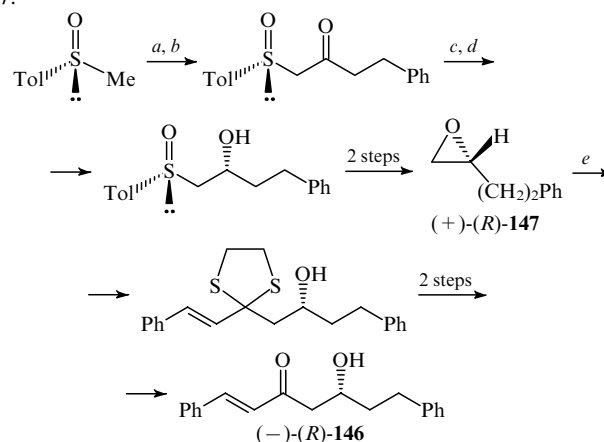


MEM is (2-methoxyethoxy)methyl.



(a) (COCl)₂, PhH; (b) $\text{N} \begin{array}{c} \diagup \diagdown \\ \text{NH} \end{array}$; (c) Ar-S(O)Me ; (d) Bu_2AlH , THF, -78°C ; (e) $\text{PhS(O)CH}_2\text{CO}_2\text{Et}$, $\text{C}_6\text{H}_{11}\text{N}$, MeCN; (f) $\text{MeOCH}_2\text{CH}_2\text{OCH}_2\text{Cl}$.

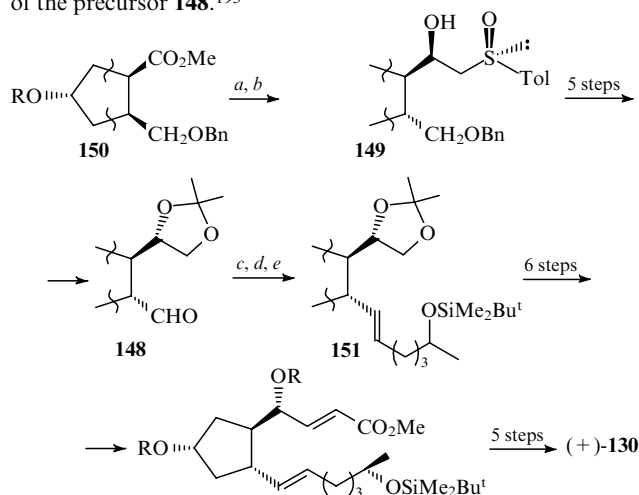
In the synthesis of (–)-(*R*)-yashabushiketol **146**, which is a rare representative of natural compounds containing a chiral hydroxy group at the β -position with respect to the carbonyl group, the hydroxysulfonyl intermediate was converted into the target ketol through the formation and cleavage of chiral epoxide **147**.¹⁹²



(a) LDA, THF, -78°C ; (b) $\text{Ph}(\text{CH}_2)_2\text{CO}_2\text{Me}$ (87%), [(+)-(*R*)];

(c) ZnCl₂; (d) Bu_2AlH ; (e) Bu^nLi , $\text{Ph} \begin{array}{c} \diagup \diagdown \\ \text{S} \end{array}$.

Syntheses of brefeldin A (**130**) performed predominantly with the use of sulfinyl-containing intermediates or auxiliary reagents are presented below. Solladie *et al.*¹⁹³ prepared a chiral cyclopentane precursor **148** with the use of enantiomerically pure 2-hydroxy sulfoxide **149**, which had been synthesised from substituted cyclopentane **150** in two steps. The formation of chiral centres at C(4) and C(15) in the brefeldin molecule was completely controlled by the sulfinyl group of the compound **149**. The (*E*)-C(10)=C(11) bond in the fragment **151** was formed using the Julia olefination with the participation of the aldehyde group of the precursor **148**.¹⁹³

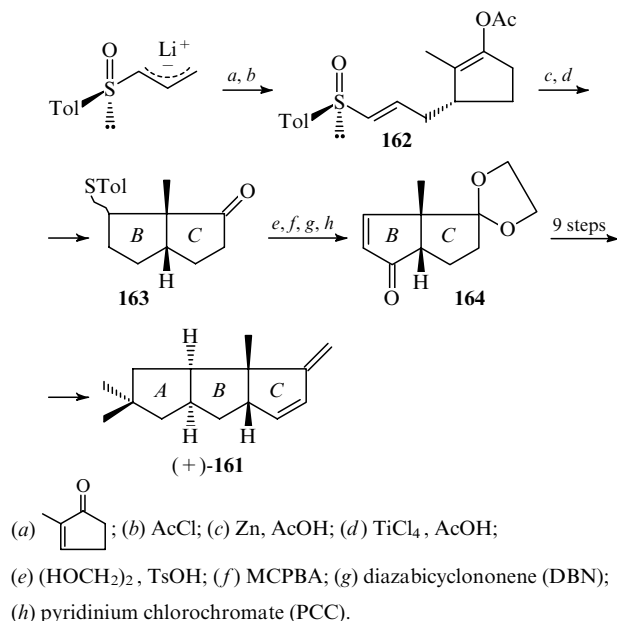


R = MEM; (a) 2 equiv. of $\text{LiCH}_2\text{S(O)Tol}$; (b) Bu_2AlH , ZnCl₂;

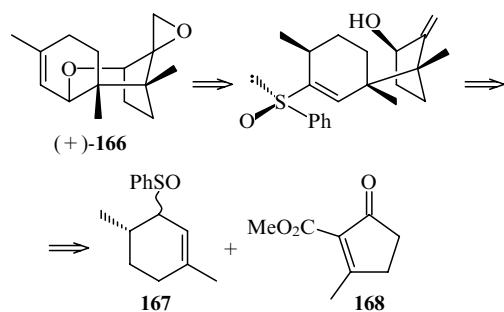
(c) $\text{PhSO}_2 \begin{array}{c} \diagup \diagdown \\ \text{OSiMe}_2\text{Bu}^t \end{array}$; (d) Ac_2O , Py; (e) Na/Hg (80%).

Two analogous schemes proposed by Corey ($\text{R}^1 = \text{MOM}$, $\text{Ar} = \text{ToI}$, $\text{R}^2 = \text{Me}$)¹⁹⁴ and Nokami ($\text{R}^1 = \text{MEM}$, $\text{Ar} = 4\text{-ClC}_6\text{H}_4$, $\text{R}^2 = \text{Et}$)¹⁹⁵ for the construction of the γ -hydroxy- α,β -unsaturated C(4)–C(15) fragment of the brefeldin molecule are based on a simplified approach using the SPAC reaction. These schemes involve the reaction of aldehyde **152** with chiral arylsulfonylacetates in the presence of piperidine as the key step.

The first line of investigations performed by Hua and co-workers^{207–211} was devoted to the addition of allylsulfinyl anions to enones. The total enantioselective synthesis of hirsutene (**161**) (a tricyclic biogenetic precursor of the polyquinanes coriolin and hirsutic acid[¶]) is a typical example of this approach. In the first stage, the (*S*)-allylsulfinyltolyl carbanion added to 2-methylcyclopent-2-en-1-one.²⁰⁷ Reduction of the reaction product **162** to sulfide followed by cyclisation afforded substituted hexahydropentalenone **163** containing the rings *B* and *C* of hirsutene. The compound **163** was transformed in several steps and then the construction of the ring *A* was completed on the basis of bicyclic enone **164**. Attempts to perform this synthesis starting from the cyclic allylsulfinyl anion **165** failed²⁰⁸ because the anions of cyclic sulfoxides of this type reacted with 2-methylcyclopent-2-en-1-one to

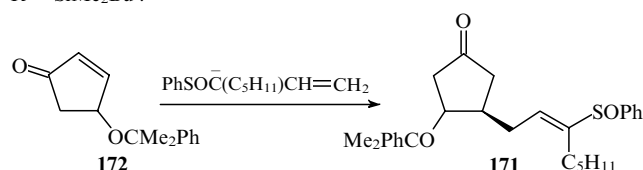
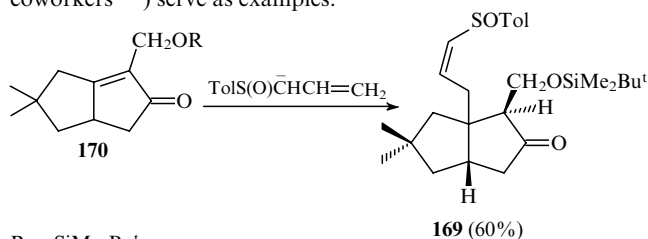


form only undesirable γ -adducts. However, the molecule of equally complicated (+)-12,13-epoxytrichocet-9-ene (**166**) possessing high biological activity was constructed starting from cyclic allylic sulfoxide **167** according to a procedure which was chosen based on retrosynthetic analysis.²⁰⁹ In this case, cyclopentenone **168** additionally activated with the methoxycarbonyl group was used. An analogous, but somewhat more complicated procedure made it possible to perform the total synthesis of (+)-pentalenene related to antitumour pentalenolactone.²¹⁰

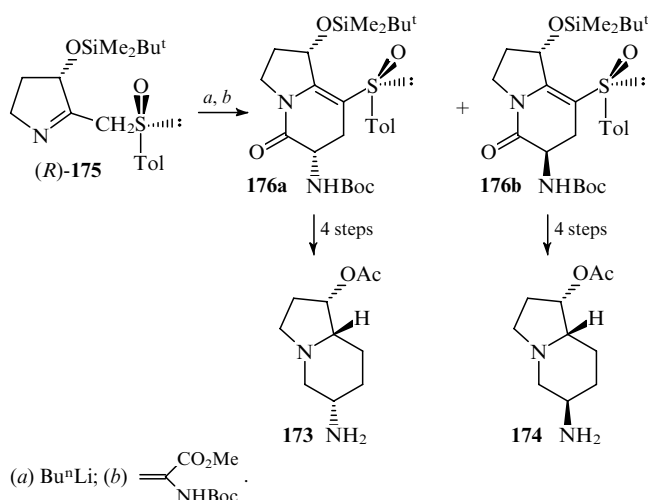


¶ Another version of the sulfonyl approach to polyquinanes is shown in Scheme 8.¹⁸⁴

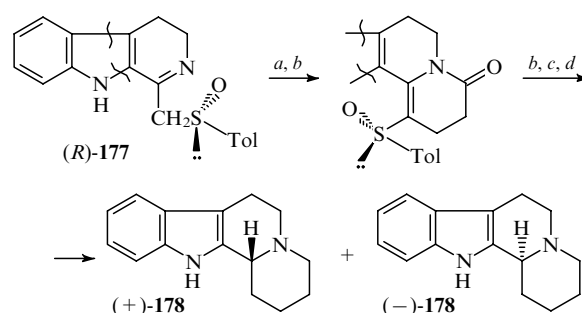
Bulky substituents in the cyclic enone do not hinder the stereoselective addition of the allylsulfinyl carbanion to the double bond. The preparation of compound **169**, which is the key intermediate in the synthesis of methyl ester of ($\pm$)-pentalenolactone E, from bicyclic enone **170**²¹¹ or the construction of the prostaglandin precursor **171** from enone **172** (Pivnitskii and coworkers²¹²) serve as examples.



The second line of investigations performed by Hua and coworkers dealt with the construction of molecules of polycyclic alkaloids based on reactions of carbanions from chiral sulfinyl ketimines with α,β -unsaturated esters followed by (sometimes synchronous) cyclisation. Thus the total syntheses of parasymphomimetic agents (–)-slaframine (**173**) and (–)-6-*epi*-slaframine (**174**) were performed starting from the sulfoxide (*R*)-**175** anion and *N*-protected methyl 2-aminoacrylate.²¹³ The diastereomers **176a** and **176b** were obtained in a ratio of 3 : 2.

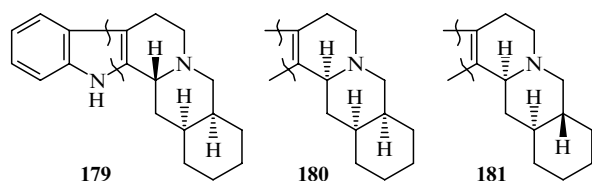


An analogous reaction of the anion of tricyclic (*R*)- α -sulfinyl ketimine **177** with methyl acrylate was used for the preparation of epimers of indolo[2,3-*a*]quinolizidine, viz., (+)- and (–)-**178** (the ratio was 1 : 1.9). The key step in the synthesis of pentacyclic

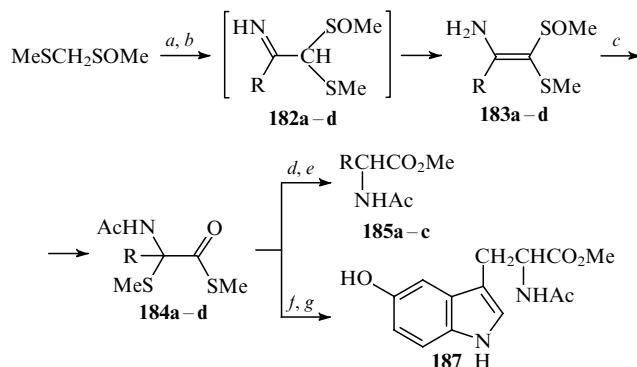


(a) LDA , CO_2Me ; (b) $\text{NaCN} \cdot \text{BH}_3$; (c) Ra/Ni ; (d) LiAlH_4 .

yohimbane alkaloids **179**–**181** involves the reaction of (*S*)-**177** with methoxycarbonylcyclohexene.²¹⁴



A general procedure for the synthesis of esters of racemic α -amino acids²¹⁵ is based on the addition of a carbanion generated from methyl methylthiomethyl sulfoxide at the C $\equiv$ N bond of nitriles. The unstable adducts **182a–d** were isomerised through a prototropic shift to form enamino sulfoxides **183a–d**. The Pummerer rearrangement under the action of Ac₂O yielded compounds **184a–d** from which racemic phenylglycine, alanine and valine derivatives (**185a–c**, respectively) were prepared. Treatment of the compound **184d** with substituted phenylhydrazine hydrochloride **186** afforded racemic *N*-acetyl-5-hydroxytryptophan methyl ester (**187**).²¹⁵

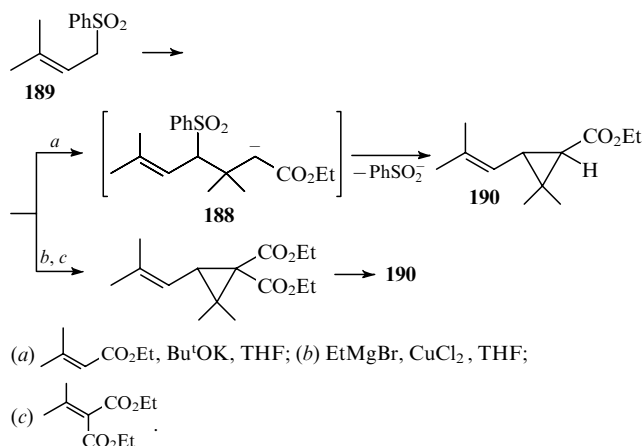


R = Ph (**a**), Me (**b**), Pr (**c**), (MeO)₂CH(CH₂)₂ (**d**); (a) NaH, THF, 20 °C; (b) RCN; (c) Ac₂O; (d) R = Ph, Me, Pr; MeOH, Et₃N; (e) Ra/Ni; (f) R = (MeO)₂CH(CH₂)₂, 4-BnOC₆H₄NHNH₂·HCl (**186**); (g) Ra/Ni, EtOH.

b. Reactions of α -sulfonyl carbanions with activated C=C bonds

Specific transformations of anionic intermediates formed as a result of addition of α -sulfonyl anions to activated double bonds have found use in the synthesis of natural products.

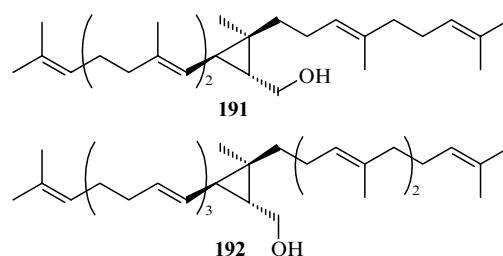
Martel *et al.*²¹⁶ found that the addition of α -sulfonyl carbanions generated from 3-methylbut-2-en-1-yl sulfones to esters of α,β -unsaturated acids afforded cyclisation products of the initially anionic intermediates rather than the usual adducts. Thus the intermediate **188** formed from sulfone **189** and ethyl 3-methylbut-2-enoate is stabilised through cyclisation with 1,3-elimination of the sulfonyl anion to produce ethyl *trans*-chrysanthemate (**190**).²¹⁷



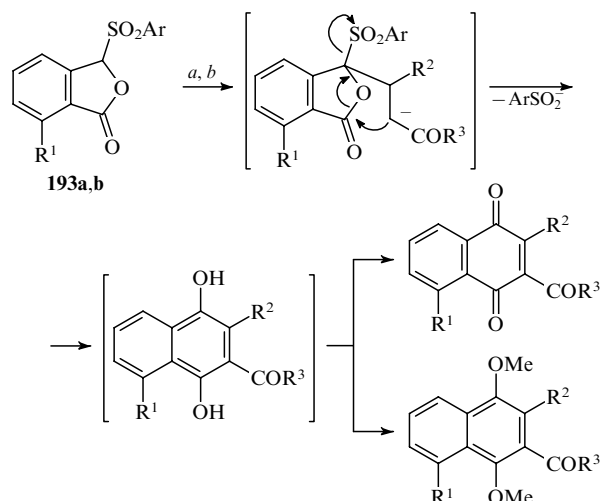
which is a component of natural insecticides, *viz.*, pyrethroids. The optimum conditions for this reaction involve the use of components taken in a ratio sulfone:THF:Bu^tOK = 1:2:3. A large number of aryl and alkyl chrysanthemates were synthesised according to this procedure.²¹⁸ Some of these compounds are more active insecticides than natural pyrethroids.

Julia and coworkers²¹⁹ prepared the ester **190** by the reaction of the sulfone **189** with ethylmagnesium bromide and then with diethyl isopropylidenemalonate.

Later on, Campbell *et al.*²²⁰ demonstrated that the reactions of anions generated from *E*-isomers of polyunsaturated sulfones with esters of polyunsaturated acids under conditions proposed by Martel and coworkers²¹⁸ were not accompanied by isomerisation of double bonds. This procedure was used for the preparation of the key compounds in the biosynthesis of terpenoids, *viz.*, (+)-presqualene alcohol (**191**) and (+)-prephytoene alcohol (**192**). In this study, the structure of natural prephytoene alcohol was also established.



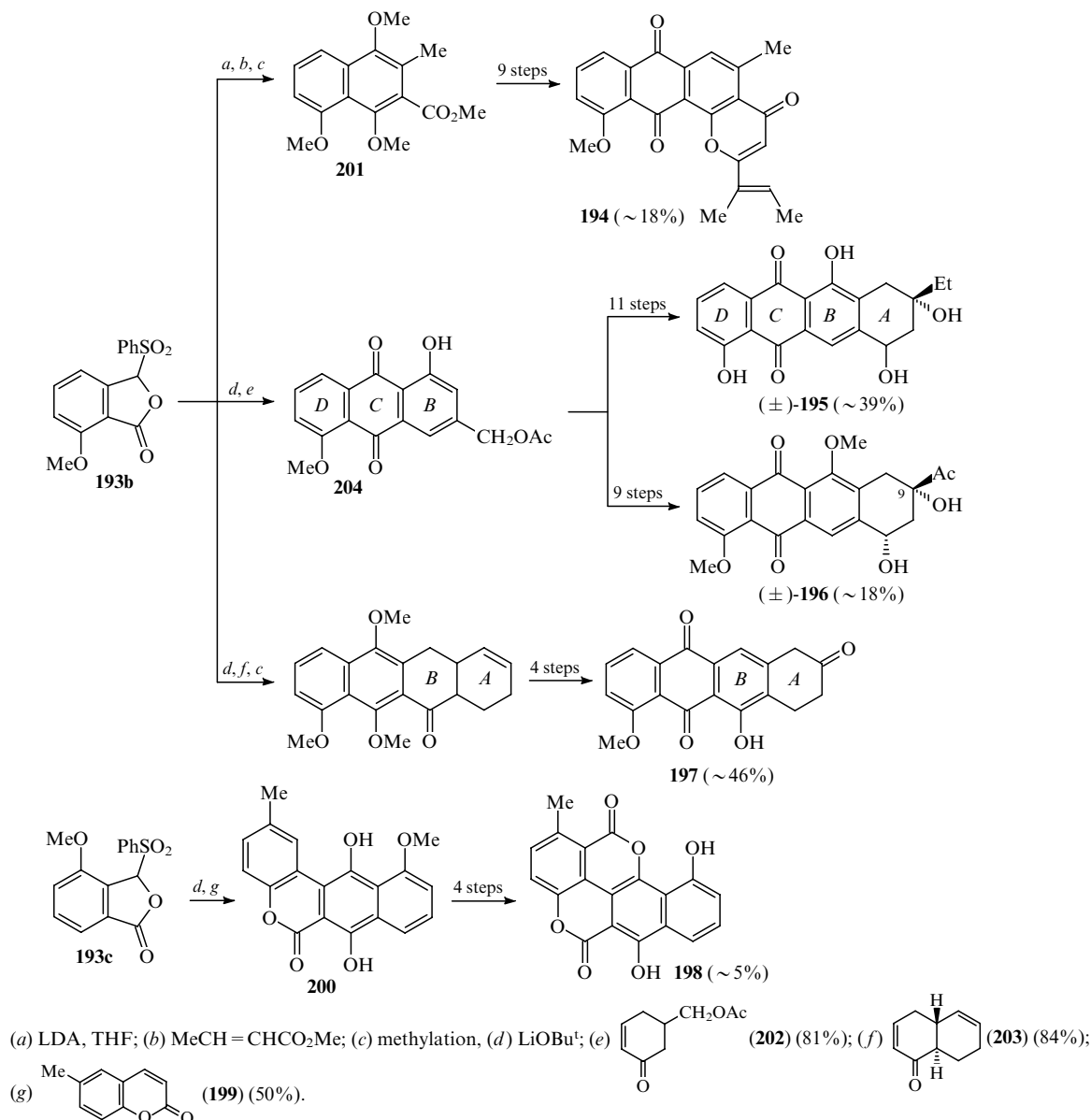
Reactions of α,β -unsaturated carbonyl compounds with α -sulfonyl carbanions generated from 3-oxo-1,3-dihydroisobenzofuran-1-yl phenyl sulfone (**193a**) ('phthalide sulfone') and its analogues play an important role in the synthesis of biologically active compounds. Hauser and Rhee²²¹ studied reactions of the model compounds **193a,b** with linear enones or α,β -unsaturated esters and demonstrated that the resulting carbanionic intermediate is stabilised in the course of cyclisation through elimination of the sulfinate anion. The resulting 1,4-dihydroxy-naphthalene is readily oxidised to naphthoquinone, whereas methylation prevents oxidation. Apparently, the driving force for this process is the formation of a thermodynamically favourable aromatic structure.



R¹ = H (**a**), OMe (**b**); R² = H, Me; R³ = OEt, Me; (a) LDA, THF, –78 °C; (b) R²CH=CHCOR³.

Owing to the possibilities of varying the structures of analogues of phthalide sulfone **193a** and, especially, of α,β -unsaturated carbonyl compounds, a flexible and rather versatile procedure was developed for stereoregular aromatic annelation, which is strictly controlled by the structures of the starting compounds. This method was successfully used by Hauser

Scheme 9

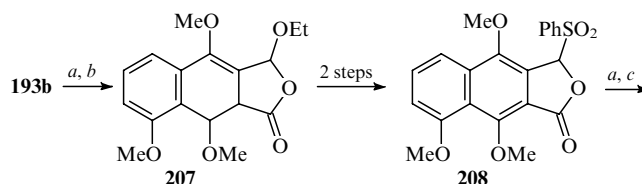


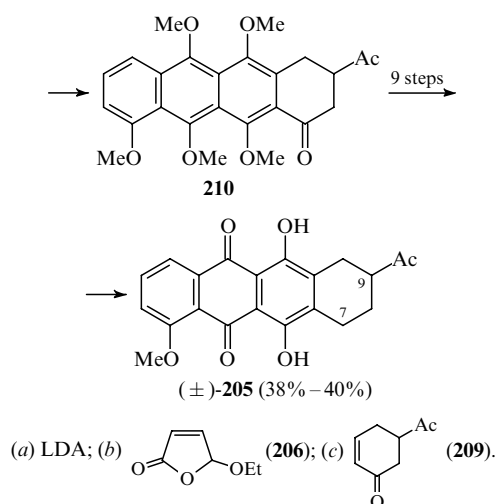
et al.^{222–234} and by other researchers^{235–238} and assumed particular importance in the synthesis of aglycones of antitumour antibiotics, for example, compounds **194**–**198**. Selected stages of the total syntheses of these compounds are shown in Scheme 9. The key reactions of the anions prepared from phthalide sulfones **193** with α,β -unsaturated carbonyl compounds generally proceed with high yields. (The exception is the reaction of phthalide sulfone **193b** with lactone **199** producing compound **200** in a yield of only 50%.) However, the multistep character of subsequent transformations impairs the efficiency of the process as a whole. Thus in the total synthesis of the antibiotic of the anthra[1,2-*b*]pyran series, *viz.*, *O*-methylkidamycinone **194**, starting from phthalide sulfone **193b** and methyl methacrylate,²²² a naphthalene derivative **201** was converted into the final antibiotic **194** in nine steps. The use of cyclic enones (such as compounds **202** or **203**) as Michael acceptors is much more efficient. Thus the reaction of phthalide sulfone **193b** with 5-acetoxymethylcyclohex-2-enone (**202**) afforded the anthraquinone derivative **204** in 81% yield.^{223, 224} Despite the fact that 11 steps were required to build up the ring *A* and to obtain the final product, *viz.*, γ -citromycinone ($\pm$)-**195**, the total yield was ~39%. A comparatively low yield of ($\pm$)-dimethyl-6-deoxydaunomycin ($\pm$)-**196** prepared from the same precursor **204** was attributed to the formation of an admixture of its C(9)-epimer in the final stage.²²⁴ The use of the simplest bicyclic enone **203** made it possible to perform a five-step

synthesis of a tetracyclic triketone **197** in good yield. The latter is a versatile precursor for the preparation of daunomycinones.²²⁵

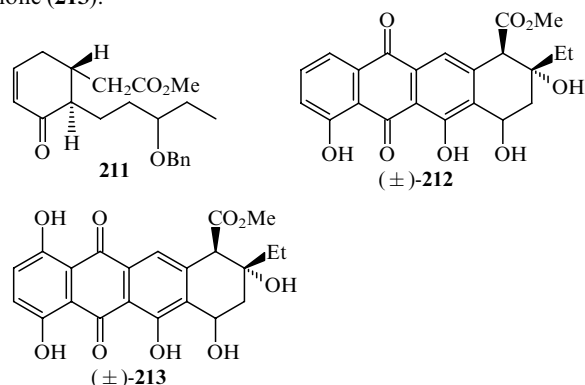
An exceptional interest in the synthesis of antibiotics of the anthracycline series (see, for example, Ref. 239) arises from their high biological activity. Thus since the 1970s²³⁹ to the present, daunomycin and adrianomycin obtainable by microbiological methods find use in medicine as antitumour drugs.²⁴⁰

Hauser *et al.*^{227, 228} have developed additional ways of improving procedures with the use of monocyclic enones. Thus the convergent synthesis of ($\pm$)-7,9-dideoxydaunomycinone (**205**) was performed in a rather high yield.²²⁷ In the first stage, the anion generated from phthalide sulfone **193b** reacted with 5-ethoxy-2,5-dihydrofuran-2-one (**206**). Then the reaction product **207** was converted into phthalide sulfone **208** in two steps. The subsequent reaction of the anion generated from **208** with 5-acetylcyclohex-2-enone **209** afforded the tetracyclic product **210**, which was converted into the target 7,9-dideoxydaunomycinone ($\pm$)-**205**.

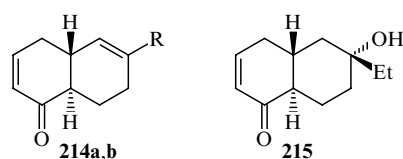




Disubstituted cyclohexenone **211** served as the starting compound in the synthesis of racemic aklavinone (**212**) and pyrromycinone (**213**).²²⁸



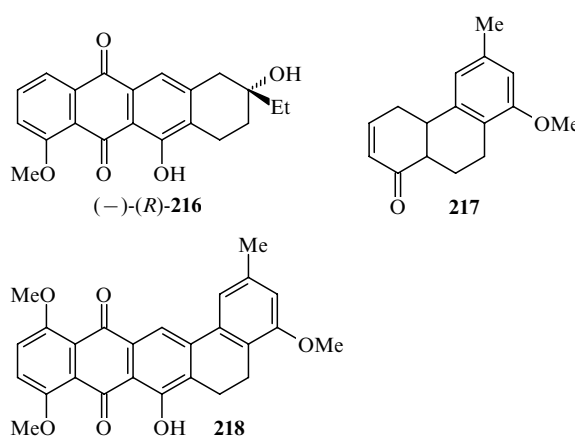
Further progress in the application of bicyclic enones to annelation was achieved^{229–234} once procedures for the synthesis of compounds **214a,b** and **215**, which contain substituents corresponding to the substituents in the rings A of anthracyclinones, had been developed.



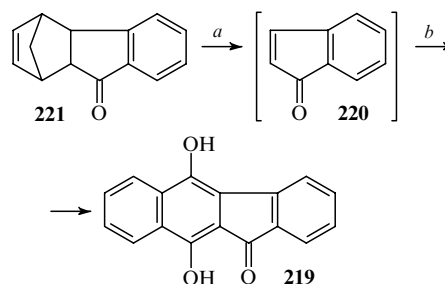
R = Ac (a), Et (b).

Thus a new more efficient procedure was proposed²³² for the preparation of racemic aklavinone [(±)-**212**] starting from readily available compounds, *viz.*, phthalide sulfone **193b** and enone **214b** (the total yield was ~ 17% with respect to 2-ethylacrolein used as the starting compound for the preparation of the enone **214b**). The first regio- and enantiospecific synthesis of a compound of the anthracyclinone series, *viz.*, the preparation of (–)-(R)-7,11-dideoxy-13-deoxydaunomycinone (**216**) from the anion of phthalide sulfone **193d** and enantiomerically pure enone **215**, was performed.²³³

Compound (±)-**218** possessing the nonlinear benzo-*a*[naphthalene skeleton was synthesised starting from phthalide sulfone **193b** and tricyclic enone **217**.²³⁴ In this study, yet another problem was solved. Thus the nature and arrangement of the substituents in the A rings of the natural pigments G2N and G2A were established.

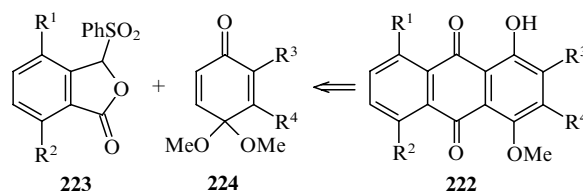


The procedure for annelation proposed by Hauser has been extended to the preparation of antibiotics containing five-membered rings. This procedure was used for the synthesis of compound **219**, which is a close analogue of kinafluorenone.²³⁵ For this purpose, the anion prepared from **193a** was brought into reaction with indenone **220**, which had been synthesised *in situ* by flash pyrolysis of its adduct with cyclopentadiene (**221**).



(a) flash pyrolysis (> 95%); (b) **193a**, LiOBu^t, –60 °C (73%).

Syntheses of natural 1,4-dihydroxyanthraquinones **222** using reactions of the anions generated from phthalide sulfones **223** with monoketals of substituted benzoquinones **224** provide other examples of annelation according to Hauser.²³⁶



R¹–R⁴ = Alk.

(±)-Daunomycinone was synthesised analogously from the sulfone **193a** and analogues of benzoquinone monoketals **224**.²³⁷ The reaction of the anion of 5,6-methylenedioxyphthalide sulfone with methyl methacrylate afforded functionally substituted naphthalenes necessary for the synthesis of lignins.²³⁸

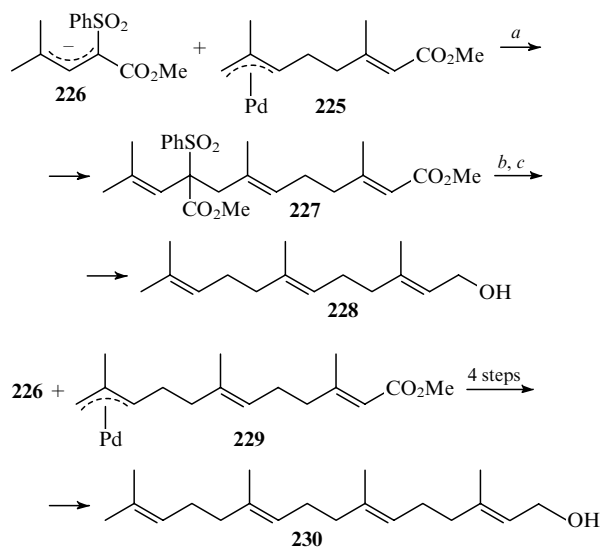
c. π -Allylic alkylation with α -sulfonyl carbanions

Among processes with the use of Pd(0) complexes, π -allylic alkylation occupies a prominent place. In these reactions, soft nucleophiles react with allylic Pd(0) complexes as the cationoid components. These complexes can be prepared from allylic compounds containing good leaving groups, such as acyloxy or sulfonyl groups. This procedure became popular due to mild reaction conditions and high stereospecificity. The reaction can be performed either with the use of stoichiometric amounts of a Pd(0) complex in a basic medium or as a catalytic process in neutral or

weakly basic media. In the latter case, the Pd(0) complex can be prepared *in situ* from a Pd²⁺ salt. The introduction of phosphine or other ligands allows one to change the regio- and stereochemistry of the reaction (see the reviews^{241–243}).

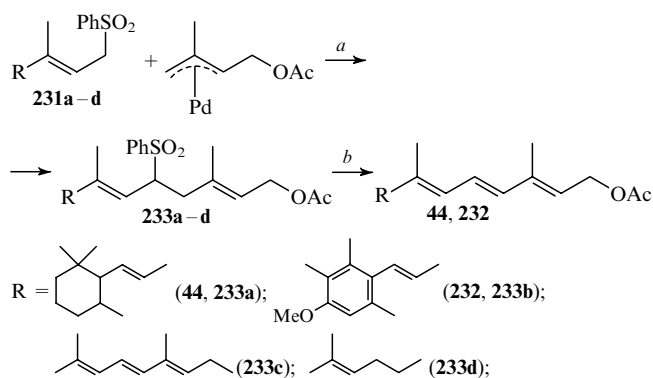
In these processes, α -sulfonyl carbanions activated with the adjacent oxo, carboxy or sulfonyl groups or (more rarely) with the allylic bond are widely used along with other C-nucleophiles.

Trost and Weber²⁴⁴ were the first to use this procedure for the synthesis of biologically active compounds and they transformed simple terpenoids into more complex compounds. The reaction of an allylic palladium complex prepared from methyl geraniate **225** with the ambident anion, which has been synthesised by the reaction of methyl 4-methyl-2-phenylsulfonylbut-3-enoate (**226**) with NaH in THF, followed by transformation of the reaction product **227** afforded farnesol (**228**). An analogous reaction of the anion **226** with the allylic Pd(0) complex **229** afforded all-*trans*-geranylgeraniol (**230**).



(a) dppe is 1,2-bis(diphenylphosphino)ethane, THF, 25 °C (65%);
(b) Bu₂AlH, MePh, –40 °C; (c) Li, EtNH₂ –78 °C.

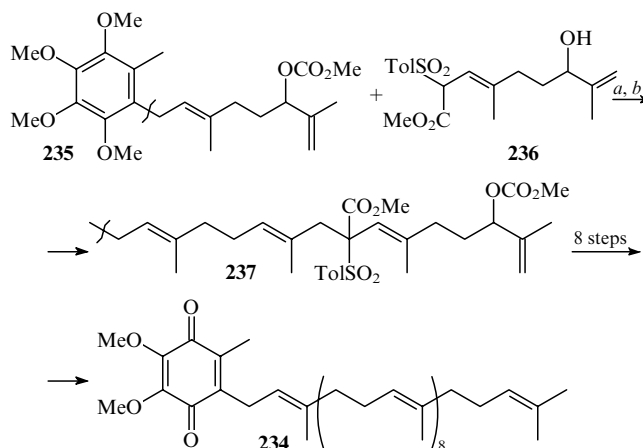
A π -allylic version of the synthesis of retinol acetate (**44**, 67% of the *trans* isomer) was carried out²⁴⁵ using the reaction of the anion generated from substituted allylic sulfone **231a** with the Pd(0) prenylacetate complex in the presence of an excess of triphenylphosphine. Its aromatic analogue **232** exhibiting antitumour activity was synthesised analogously. In the case of sulfones containing acyclic substituents R, the reactions stopped at the stage of formation of compounds **233c,d**.



(a) NaH, THF, PPh₃; (b) EtONa, EtOH.

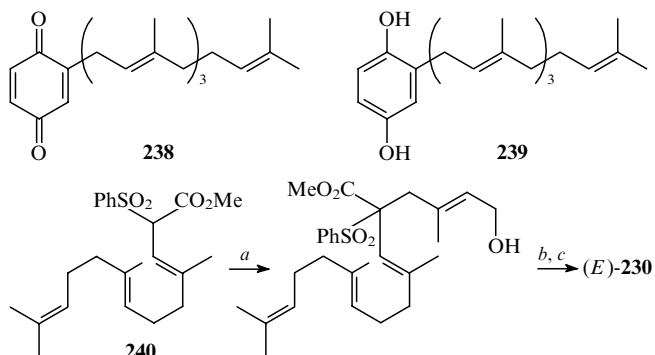
Tsuji was the first to propose a catalytic version of this reaction^{242,246} and he recommended to employ *O*-methoxycarbonyl as the leaving group. This procedure was used for the preparation²⁴⁷ of ubiquinone-10 (**234**), which is the coenzyme Q₁₀ exhibiting cardiovascular activity, and its analogues. Compound

235 containing an allylic *O*-methoxycarbonyl group was brought into the reaction with the anion of an activated sulfone **236** containing an allylic hydroxy group, which was employed to form a new allylic *O*-methoxycarbonyl group in the intermediate **237**. The iterative reaction with the sulfone **236** and the formation of the MeO₂CO group made it possible to build up a polyunsaturated chain. The last stage of the process involved oxidation of the aromatic ring to the quinoid one.



(a) 5 mol. % of Pd(PPh₃)₄, THF; (b) MeOCOC(=O)Et, Et₂NC₆H₄, Py, PhH.

Natural compounds exhibiting analgesic activity, *viz.*, tetraprenylquinone **238** and -quinol **239**, were prepared analogously.²⁴⁸ The synthesis of *trans,trans,trans*-geranylgeraniol (**230**) from α -sulfonyl-substituted ester **240** and oxirane **241** was also performed using the catalytic version.²⁴⁹ In this scheme, the metal-complex catalysis was used for the regiospecific opening of the oxirane ring.

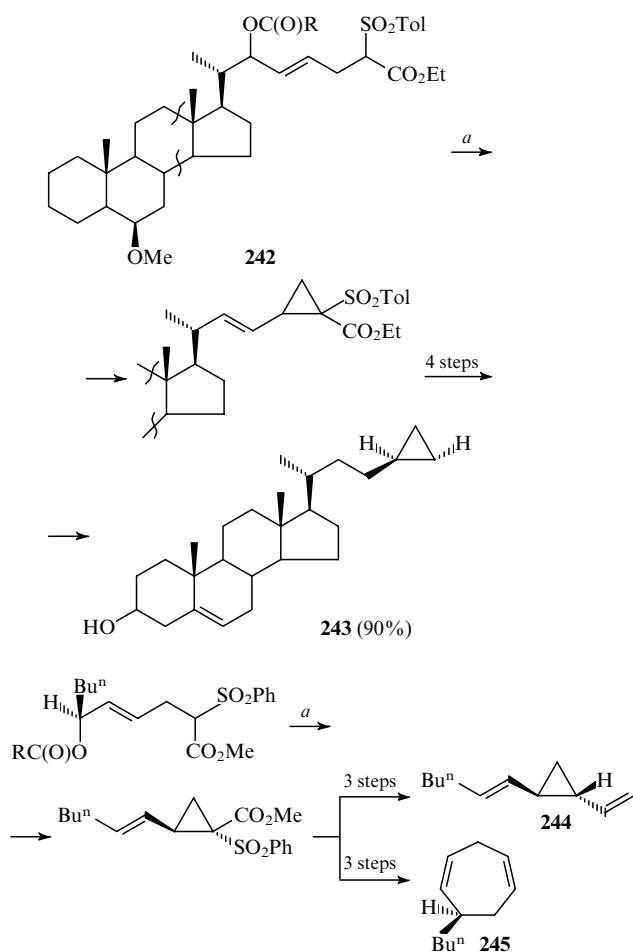


(a) **241**, 5 mol. % of Pd(PPh₃)₄, THF, 25 °C (90%);

(b) PhSH, Cs₂CO₃; (c) LiBHEt₃, THF, 5 mol. % of PdCl₂(dppp)
[dppp is 1,3-bis(diphenylphosphino)propane] (100% *E*).

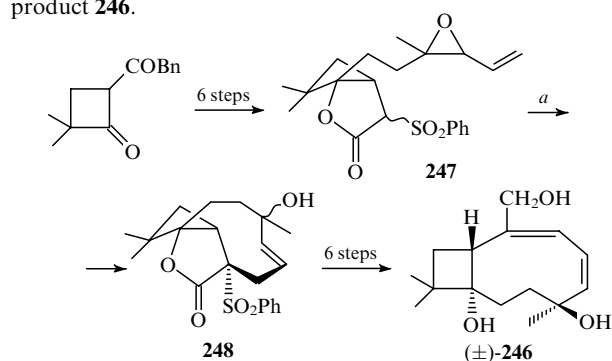
The catalytic procedure has assumed utmost importance in intramolecular cyclisations, which offers outstanding possibilities for the construction (including diastereocontrol) of carbo- and heterocycles (see the reviews^{250,251}).

Thus the diastereoselective introduction of a cyclopropane ring into the steroid molecule was performed by the reaction of the carbanion generated from the sulfonyl(ethoxycarbonyl) fragment of compound **242** with the π -allylic Pd complex generated in the same molecule. The final product, *viz.*, glaucasterol (**243**), contains a three-membered ring at C(24)–C(25).²⁵² 2-(Hex-1-en-1-yl)-1-methoxycarbonyl-1-phenylsulfonylcyclopropane was synthesised analogously. The latter compound served as the starting material for the synthesis of dictyoptene A (**244**) containing a three-membered ring and of a seven-membered dictyoptene B (**245**).²⁵³



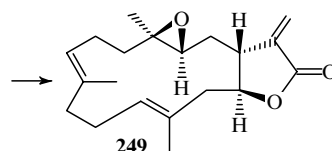
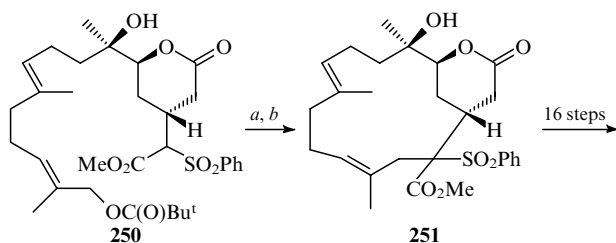
R = 2,4-Cl₂C₆H₃; (a) DBU, THF, Pd(dppe)₂.

Examples of the construction of more complex carbocycles are considered below. Bicyclic (±)-punctaporonin **B** (**246**) was synthesised in 12 steps starting from substituted cyclobutanone.²⁵⁴ The palladium-catalysed reaction of the allyloxirane fragment of compound **247** with the activated α-sulfonyllactone fragment afforded the intermediate **248**, which was converted into the target product **246**.



(a) Pd(Ph₃P)₄, dppe, THF, 60 °C.

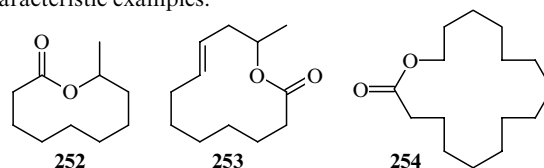
In the synthesis of 14-membered (±)-isolobophytolide (**249**), the methoxycarbonyl(phenylsulfonyl) carbanion served as the anionic component of the initial compound **250** and the pivalate



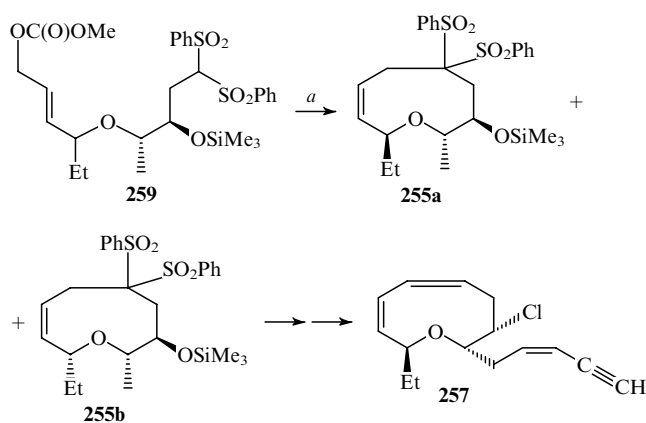
(a) *O,N*-bis(trimethylsilyl)acetamide, Pd(Ph₃P)₄, dppe, THF; (b) Bu₄NF.

anion served as the leaving group. The resulting macrocyclic intermediate **251** was transformed into the target product **249**.²⁵⁵

Cyclisation catalysed by palladium complexes is of particular importance for the preparation of medium-size heterocycles, which are widespread in nature, but which have previously been difficultly accessible.^{256–261} The construction of the key intermediates in the synthesis of natural lactones, viz., 10-membered phoracantholide (**252**),²⁵⁶ 12-membered recifeolide (**253**)²⁵⁷ and 16-membered exaltolide (**254**),²⁵⁸ from acyclic precursors serve as characteristic examples.

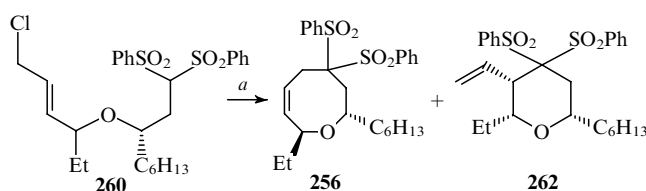


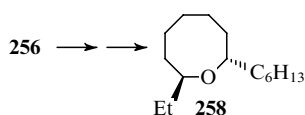
The construction of nine- and eight-membered functionally substituted cyclic ethers **255a,b** and **256**, which are precursors of oxonins **257** and **258** isolated from the algae *Laurencia*, presented a substantially more difficult problem. The regio- and stereochemical direction of cyclisation of the acyclic precursors **259** and **260** is determined by the site of attack of the anion generated from the sulfone on the allyl palladium fragment and depends on the nature of the leaving group and, especially, on the ligand used. Thus the methoxycarbonyloxy group and triethyl phosphite appeared to be the best leaving group and ligand, respectively, for the ring closure in compound **259** required for the construction of the skeleton of nine-membered brasilenyne (**257**). The ratio of the cyclisation products, viz., *trans-trans*-**255a** (similar to the natural isomer) and undesirable *cis-trans*-**255b**, was 14 : 1.²⁵⁹



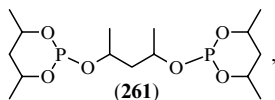
(a) 5 mol. % of Pd₂(dba)₃ (dba is dibenzylideneacetone), 50 mol. % of P(OEt)₃, CHCl₃, THF.

A chloride anion and bisphosphite **261** appeared to be the best leaving group and ligand, respectively, in the stereoconvergent synthesis of compound **256**, which is a precursor of enantiomerically pure (–)-lauthisan (**258**).²⁶⁰ Because of the formation of



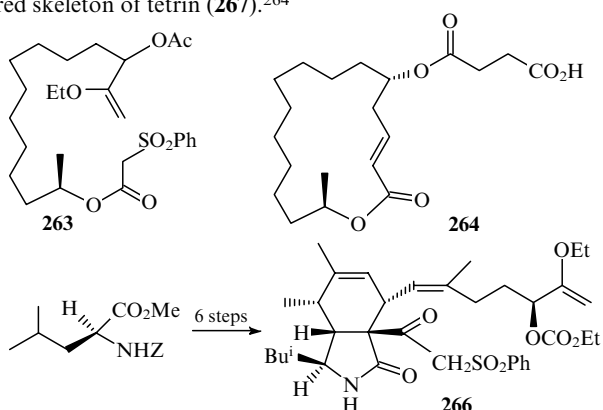


(a) 5 mol. % of $\text{Pd}_2(\text{dba})_3$, CHCl_3 , KH ,
THF–dioxane, 80 °C.

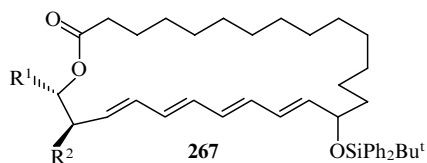


the six-membered cyclic products **262**, the yield of the eight-membered reaction product **256** was only 70%.²⁶⁰

The construction of more complex heterocycles, viz., macrocides of the cytochalasin series, which possess high membrane-transport and a broad spectrum of other biological activities, presented a particularly interesting problem. Trost and coworkers performed a 12-step synthesis of the model antibiotic A 22667718 (**264**) starting from undecynal *via* the intermediate **263**,²⁶² a 9-step synthesis of (–)-aspothalasin [(–)-**265**] from *N*-protected leucine ester *via* the precursor **266**²⁶³ and construction of the 26-membered skeleton of tetrin (**267**).²⁶⁴

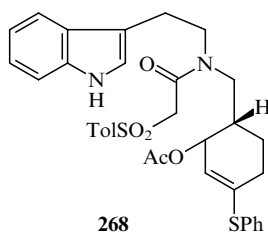


Z = COOBn.



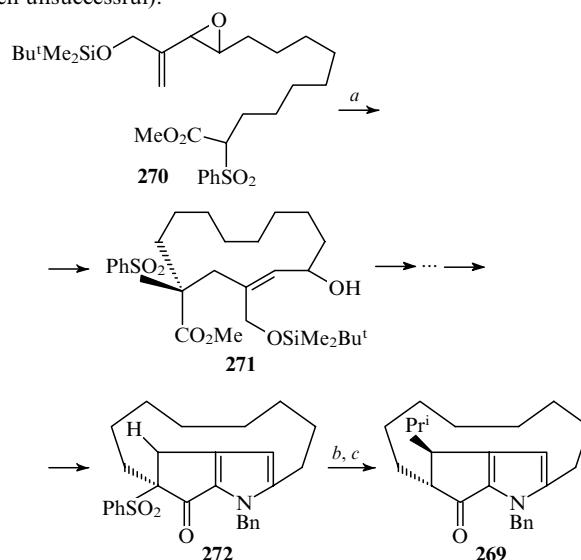
$\text{R}^1, \text{R}^2 = \text{H}, \text{Me}$.

A precursor of pentacyclic allyohimbane was synthesised analogously using the Pd(0)-catalysed ring closure in compound **268** with the acetoxy group serving as the leaving group.²⁶⁵



A 12-step synthesis of the skeleton of the macrocyclic anti-tumour compound roseophillin (**269**) is yet another example of the high efficiency of palladium-catalysed cyclisation.²⁶⁶ Acyclic

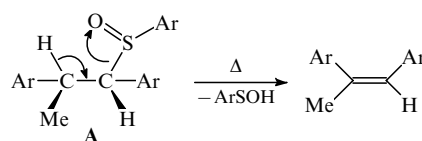
compound **270** was transformed into the cyclic precursor **271** by the reaction of the methoxycarbonylsulfonyl fragment with the allylpalladium complex incorporating the oxirane ring. The groups that activate the anionic centre were not removed following cyclisation and they were employed in subsequent transformations. Thus the ester group was used in the construction of tricyclic sulfone **272**. The benzenesulfonyl group in compound **272** is homoallylic and hence it was readily eliminated in the presence of Bu^tOK as sulfenic acid. Simultaneously, the isopropyl group was attached to the adjacent carbon atom by the action of dimethylisopropylzincmagnesium chloride on the $\text{C}=\text{C}$ bond of the enone formed (attempts to use more traditional cuprates have been unsuccessful).



(a) $[\text{Pd}(0)]$ (85%); (b) an excess of Bu^tOK ; (c) $\text{Me}_2\text{Pr}^i\text{ZnMgCl}$ (51%).

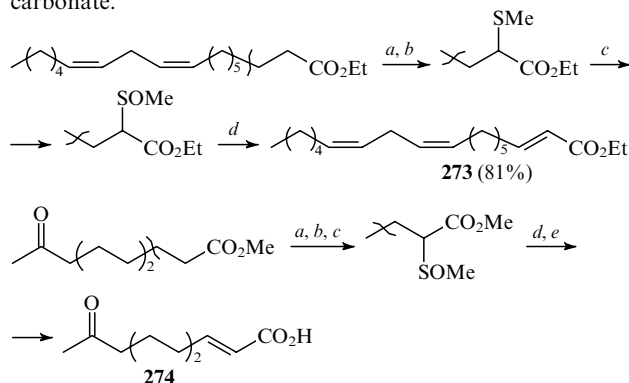
IV. Formation of $\text{C}=\text{C}$ bonds by thermolysis of sulfoxides

In many cases, thermal elimination of sulfenic acid from sulfoxides leads to the formation of (*E*)- $\text{C}=\text{C}$ bonds. In 1960, Kingsbury and Cram²⁶⁷ suggested that at moderate temperatures this process occurs according to a concerted mechanism *via* a transition state **A**. More recently,²⁶⁸ this suggestion was confirmed by kinetic studies.



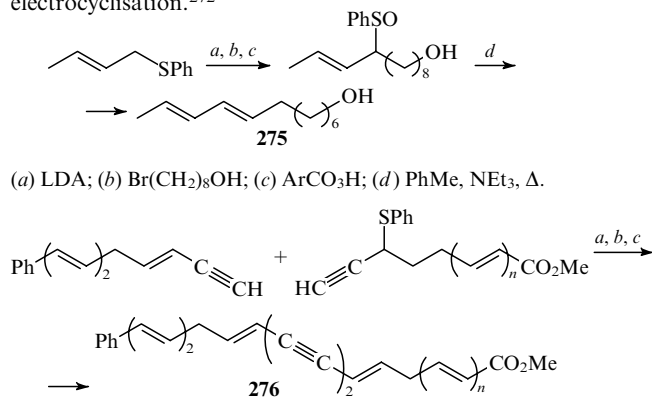
A modification of this reaction proposed by Trost *et al.*^{33–35, 40, 269, 270} has been widely used predominantly for the introduction of (*E*)- $\text{C}=\text{C}$ bonds at the α, β -position with respect to the carbonyl groups of ketones or esters. This procedure is convenient because a one-pot sulfonylation–sulfinylation–dehydrosulfonylation sequence can be used. Initially, an alkylthio group is introduced at the α -position with respect to the electron-withdrawing group under the action of disulfide in a basic medium. The alkylthio group is readily oxidised to the sulfinyl group, which is removed by thermolysis, most commonly, upon boiling in toluene. All steps are carried out under mild conditions; the presence of functional groups in the molecule does not hinder this process. The temperature required for dehydrosulfonylation depends on the substrate structure. Sometimes, it is necessary to add a thiophilic scavenger. This method for the directed introduction of (*E*)- $\text{C}=\text{C}$ bonds advantageously supplements the Julia olefination and dehydrosulfonylation of homoallylic sulfones.

The synthesis of components of bee pheromones is the first example of the use of the sulfonylation–sulfinylation–dehydro-sulfonylation sequence for the preparation of natural compounds.²⁷⁰ Ethyl linoleate served as the starting compound for the preparation of the attractant **273**. (*E*)-9-Oxodec-2-enoic acid (**274**) (the queen substance, *viz.*, the attractant of the queen bee and simultaneously the pheromone of termites) was prepared from an azelaic acid ester. In both cases, thermolysis was performed by boiling in toluene with the addition of calcium carbonate.



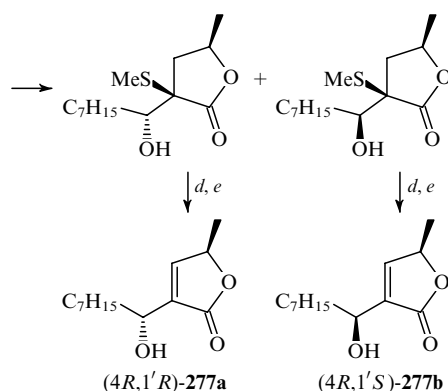
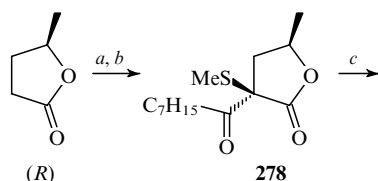
(a) cyclo-C₆H₁₁NPr⁺Li; (b) MeSSMe, THF, HMPT, –78 °C; (c) oxidation; (d) PhMe, CaCO₃, 110 °C, 16 h; (e) H₃O⁺.

The sulfinyl groups located at the allylic or propargyl positions are also readily eliminated under conditions of thermolysis because the resulting conjugated diene and enyne systems are thermodynamically favourable. This procedure was used for the preparation of dodeca-8,10-dien-1-ol (**275**)²⁷¹ (the major component of the pheromone of apple fruit moth) and polyunsaturated esters **276**, which are the key compounds in the synthesis of natural unsaturated endiandric acids involving mild cascade electrocyclicisation.²⁷²



(a) LDA; (b) Br(CH₂)₈OH; (c) ArCO₃H; (d) PhMe, NEt₃, Δ.

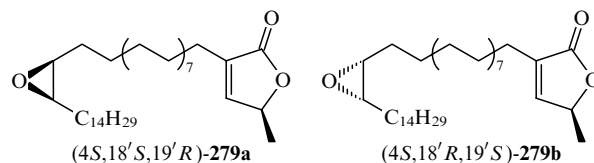
Endocyclic C=C bonds can also be readily constructed by this procedure. For example, all four possible enantiomers of the natural CoA inhibitor, *viz.*, acaterin (**277**), with an acetogenin-type skeleton were prepared. The latter is a promising anti-atherosclerosis drug.²⁷³ The (4*R*,1'*R*) absolute configuration was assigned to the natural inhibitor. Both compound (+)-**277a** and its C(1')-epimer **277b** were prepared by thermolysis (after oxida-



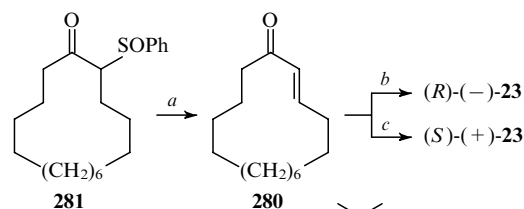
(a) LDA, MeSSO₂Me; (b) LDA, C₇H₁₅COCl; (c) NaBH₄, THF, H₂O; (d) oxidation; (e) PhMe, CaCO₃, Δ, 3 h.

tion) of substituted valerolactones isolated from a mixture of reduction products of compound **278**. The second pair of epimers of the compound **277** was synthesised according to the same procedure starting from (*S*)-γ-valerolactone.

An analogous procedure for the introduction of the endocyclic C=C bond was used²⁷⁴ in the synthesis of compounds **279a,b**, which were supposed to correspond to stereoisomers of a more complex acetogenin, *viz.*, epoxyrollin A. However, the ¹³C NMR and mass spectra of both stereoisomers **279a,b** differed from those of the natural product.

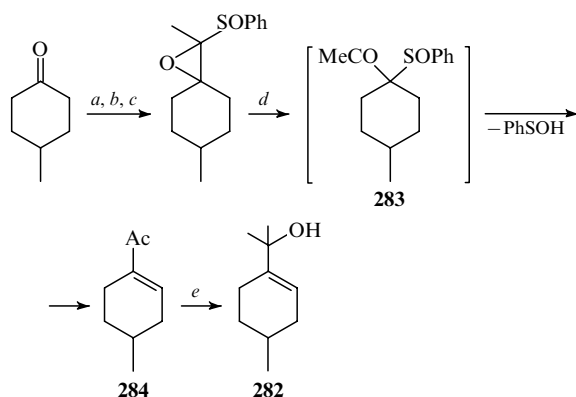


A short elegant synthesis of (+)-(*R*)- and (–)-(*S*)-muscones **23** involved asymmetric methylation of the C=C bond of the enone **280** in the presence of D- or L-camphor derivatives, respectively.²⁷⁵ The enone **280** was prepared by elimination of benzenesulfenic acid from the oxo sulfoxide **281**.



(a) PhH, CaCO₃, Δ (83%); (b) MeLi, CuI₂, PhMe, THF (*ee* 100%); (c) MeLi, CuI₂, PhMe, THF (*ee* 100%).

8-Hydroxymenth-3-ene (**282**), which is a component of mint essential oil, was prepared according to a general procedure for the transformation of saturated ketones to enones proposed by Taber and Gunn.²⁷⁶ In the first step, α-chloroethylsulfinyl carbanion was added to the carbonyl group of 4-methylcyclohexanone to form epoxide. When distilled, the latter underwent spontaneous isomerisation to give unstable oxo sulfoxide **283**, which readily eliminated sulfenic acid. The addition of MeLi to enone **284** completed the process.

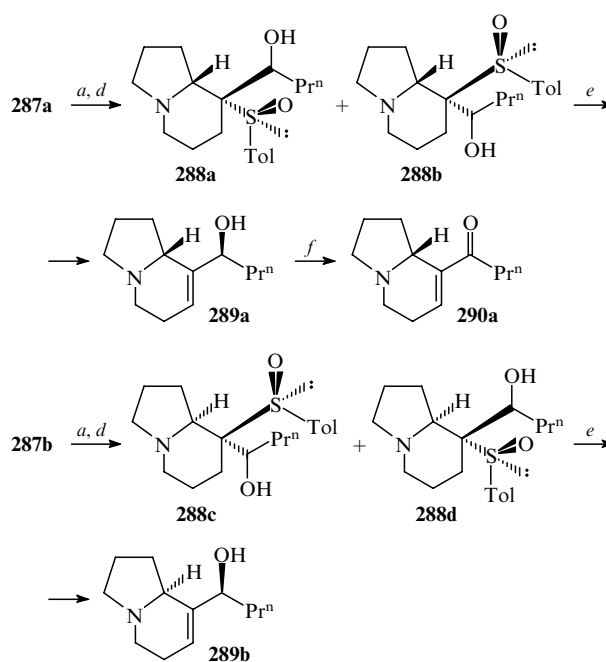
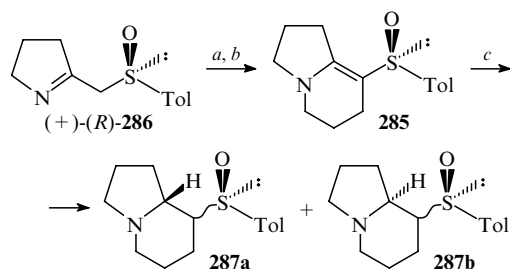


(a) LDA, THF; (b) MeCH(Cl)SOPh; (c) NaOH (90%);
(d) Δ , CaCO₃; (e) MeLi.

If the sulfonyl group is located in the aliphatic chain, the direction and the rate of hydrogen abstraction upon thermolysis depend predominantly on its acidity.^{35,269} However, thermolysis of steroid sulfoxides is a stereocontrolled process due apparently to the unique features of this system of rigidly fused rings. Thus attempts to introduce the C(15)=C(16) bond into the estrone molecule according to a conventional procedure [starting from C(16)-selenoxide²⁷⁷] failed, but this bond was constructed upon prolonged heating of the methyl ether of C(16)-(phenylsulfinyl)estrone in the presence of triphenyl phosphite, which is an active thiophilic scavenger.⁴⁰ Elimination of sulfenic acid from the A ring of 5 α - or 5 β -cholestanes occurred under standard conditions.²⁷⁸ The dependence of the direction and rate of thermolysis on the stereochemistry of the sulfur atom was observed for the first time in the case of bulky thermally stable (*R*)- and (*S*)-adamantylsulfinyl groups, which are not able to undergo stereomutation. This made it possible to develop procedures for the selective synthesis of difficultly accessible 5 α - or 5 β -cholest-2-enes and cholest-3-enes.²⁷⁶

The formation of C=C bonds by thermolysis of sulfoxides was also used in more sophisticated synthetic sequences. For example, this reaction served as a stage in the construction of brefeldin A (**130**)^{181,183} and in the synthesis of hirsutene²⁰⁷ (in the latter case, thermolysis was carried out in an alkaline medium according to a procedure reported previously²⁷⁹). Other examples will be considered below.

In the course of the total enantioselective synthesis of indolizine alkaloids elaeokanines A and B, Hua *et al.*²⁸⁰ used a large number of approaches based on reactions of sulfinyl-containing intermediates. Enamino sulfoxide **285** was prepared by alkylative annelation in the reaction of 1,3-diiodopropane with the anion of (+)-(*R*)-sulfinyl ketimine **286**. Reduction of the reaction product afforded a mixture of all four possible epimeric indolizine sulfoxides represented in pairs as **287a** and **287b**. The reaction of each of these epimers with butanal in the presence of lithium diisopropylamide proceeded quantitatively, the C(8a) chiral centre, which is essential for the subsequent synthesis, remaining unchanged. Thermolysis of a 2 : 1 mixture of hydroxy sulfoxides **288a** and **288b** gave the single product, *viz.*, hydroxyindolizine **289a** with the



(a) LDA; (b) I(CH₂)₃I; (c) NaBH₄, **287a** : **287b** (1 : 1); (d) PrⁿCHO;
(e) 110 °C, PhMe (~80%); (f) PCC (>90%).

C(7)=C(8) bond. Oxidation of the hydroxy group of **289a** resulted in (+)-elaekanine A (**290a**). (–)-Elaekanine B (**289b**), which is (unlike elaeokanine A) a hydroxy derivative, was prepared by thermolysis of hydroxy sulfoxides **287c,d** obtained by the reaction of butanal with the diastereomers **287b**.

V. Syntheses based on reactions of unsaturated sulfones and sulfoxides

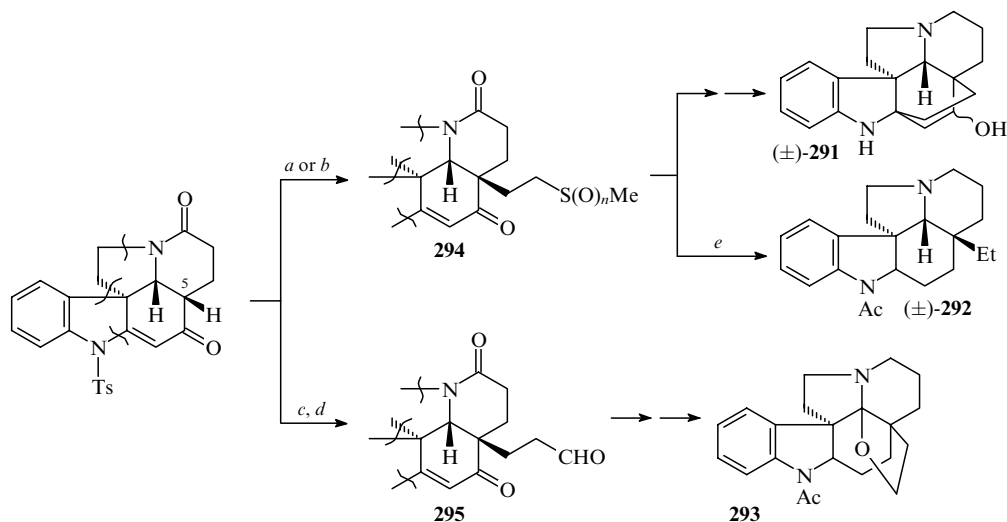
1. Addition at the C=C bonds

a. Addition of C-nucleophiles

The synthesis of racemates of alkaloids (**291**–**293**) of the *Aspidosperma* family from a single pentacyclic precursor provides an example of the use of unsaturated sulfones and sulfoxides as acceptors of C-nucleophiles for the transformation of the basic skeleton, which has been constructed beforehand.^{281–283} Owing to the high acidity of the hydrogen atom at C(5) of the enone fragment, the carbanion can readily be generated and involved in the Michael addition to methyl vinyl sulfone, methyl 1-methylthiovinyl sulfoxide or methyl vinyl sulfoxide. Subsequent modifications of the adducts **294** and **295** involved the formation of additional rings in the alkaloids 4-hydroxyaspidofractinine (**291**) and 1-acetylaspidoalbidine (**293**) and the introduction of the ethyl group at position 5 in 1-acetylaspidospermidine **292** (Scheme 10).

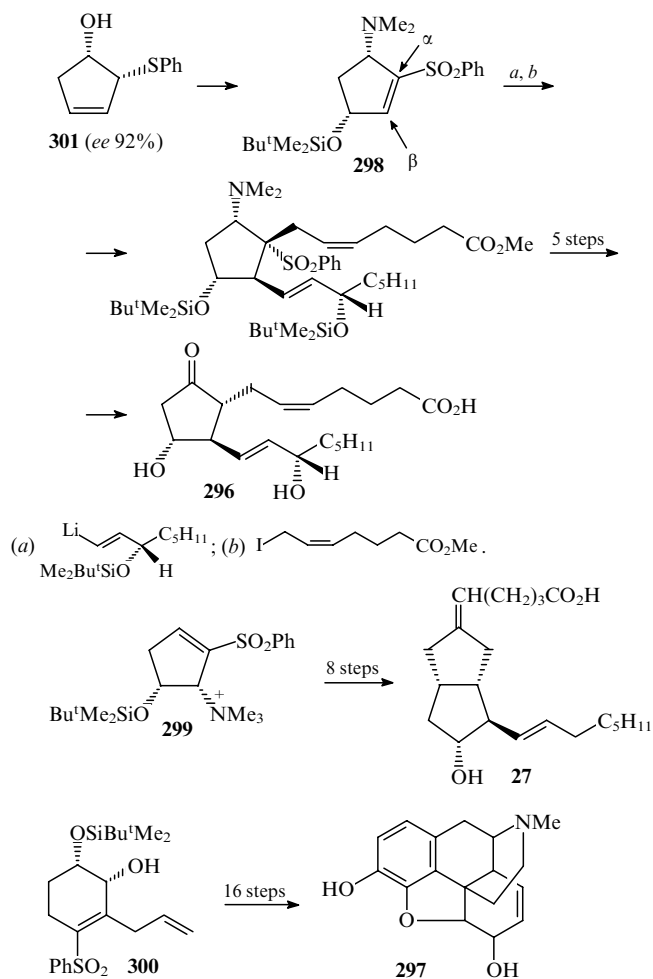
Vinyl sulfones have found substantially wider application due to the fundamental studies of Fuchs and coworkers, which have been surveyed in detail in their reviews.^{23,24} Hence, these studies will be considered in this review only briefly. Fuchs and coworkers have developed convenient procedures for the synthesis of substituted cycloalkenyl sulfones, including enantiomerically pure sulfones, containing a free or substituted hydroxy group at the γ -position. In the case of vinyl sulfones, unlike enones, the attack of even hard nucleophiles (for example, alkylolithium) occurs exclusively at the C=C bonds following a Michael addition. Owing to the high nucleophilicity of the resulting α -sulfonyl carbanion compared to enolate, the addition can be combined with a subsequent reaction of the newly formed α -sulfonyl carbanion with an internal or external electrophile resulting in additional functionalisation. The presence of γ -hydroxy groups in these vinyl sulfones allows one to control the stereochemistry of the process.

Scheme 10



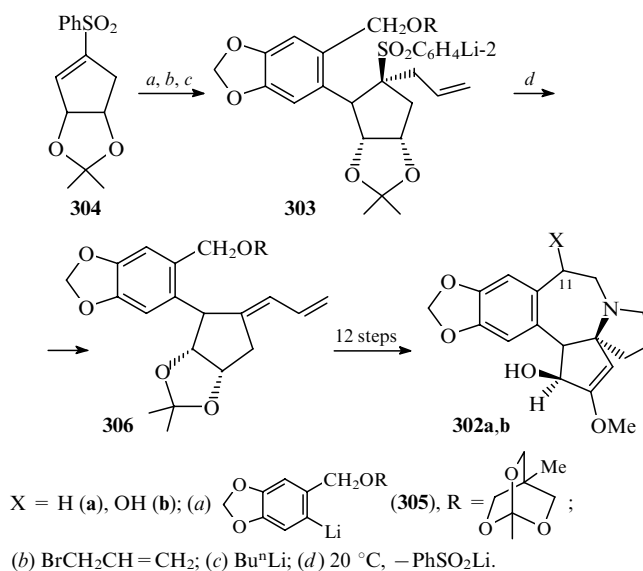
(a) $\text{CH}_2=\text{CHSO}_2\text{Me}$, Bu^tOK , Bu^tOH , $n = 2$; (b) $\text{CH}_2=\text{CHSOMe}$, LDA , $n = 1$; (c) $\text{CH}_2=\text{C}(\text{SOMe})\text{SMe}$, LDA ; (d) HClO_4 , H_2O ; (e) Ra/Ni , $n = 1$.

The scheme given below outlines in general convergent total syntheses of natural or related compounds, *viz.*, (–)-prostaglandin E_2 (**296**),²⁸⁴ (+)-carbacyclin (**27**)²⁸⁵ and (±)-morphine (**297**),²⁸⁶ carried out by Fuchs and coworkers. The key steps of these syntheses involve β -addition– α -alkylation of cycloalkenyl sulfones **298**–**300** (in the scheme, the sites of the α - and β -attacks are indicated by arrows).



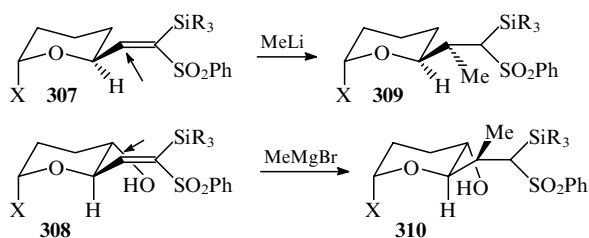
The synthesis of prostaglandin **296** from the vinyl sulfone **298** involves only seven steps (the total yield was 13% with respect to 2-phenylthiocyclopent-3-enol **301** with *ee* 92%).²⁸⁴ The prepara-

tion of racemic cephalotaxine **302a**,^{287, 288} is worthy of notice as an example of more complicated syntheses. The scheme under consideration is of interest from the viewpoint of the diversity of chemical transformations. The lithiated intermediate **303** prepared from vinyl sulfone **304** by consecutive reactions with the lithium derivative **305**, allyl bromide and then with Bu^nLi contains the homoallylic sulfonyl group, which is spontaneously eliminated as lithium sulfinate. The *exo*-1,3-diene group of the reaction product **306** is used in one of the major steps of subsequent transformations to produce cephalotaxine, *viz.*, for the construction of the seven-membered heterocycle. A modification of this procedure afforded 11-hydroxycephalotaxine (**302b**). However, this method, despite its elegant character, is unsuitable for the preparation of optically active forms of compounds **302a,b**.^{287, 288}

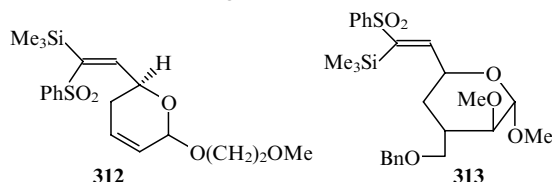
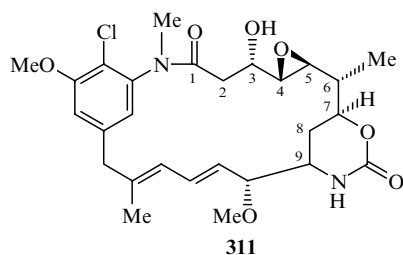


A procedure for the 'heteroconjugate addition' developed by Isobe²⁸⁹ made it possible to solve a very important problem of the efficient stereocontrol in the construction of new acyclic C–C bonds enabling, simultaneously, further carbon-chain elongation. This method was tested using model pyranosides containing α -silylated vinylsulfonyl substituents at C(5). In this case, D-glucopyranose derivatives serve as chiral pools.

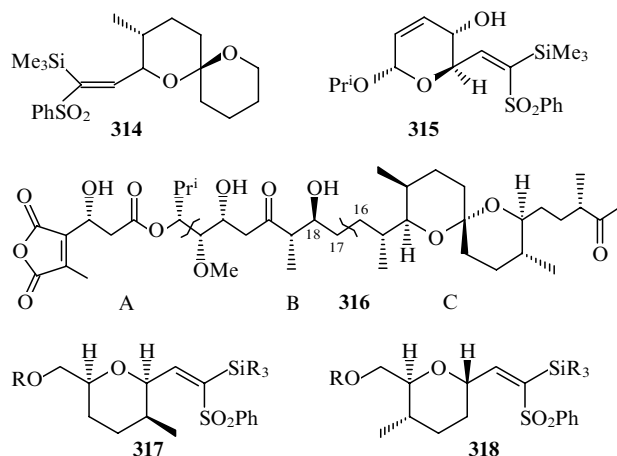
Owing to the bulky α -silyl substituent, the substrate molecule adopts a conformation in which the direction of the attack of the nucleophilic reagent [*syn* or *anti* with respect to the H atom at C(5)] depends both on the nature of the reagent and the sub-



stituents in the pyran ring, which can form chelates with nucleophiles. In the absence of polar substituents (compound **307**), the reaction with alkyllithium proceeds exclusively as *syn*-alkylation.²⁹⁰ The presence of the hydroxy group at C(4) in compound **308** and the use of a Grignard reagent provide conditions for exclusive *anti*-alkylation due to the formation of a chelate with the reagent.²⁹¹ Subsequent chain elongation in the intermediates **309** and **310** was performed predominantly by alkylation of the α -sulfonyl carbanion after desilylation. This method was used for the introduction of the *syn*-methyl group at position 6 in the total syntheses of maysine and *N*-methylmaysenine²⁹² as well as of racemic maytansinol (**311**)²⁹³ and (–)-maytansinol.²⁹⁴ Vinyl sulfones **312** and **313** were used as the starting compounds for the construction of the C(4)–C(9) fragment. In the total synthesis of okadaic acid (**94**), vinyl sulfones **314** and **315** were used for the introduction of the *anti*-C(13)-methyl group and the *syn*-C(29)-methyl group into the segments *A*¹⁴⁵ and *C*,¹⁴⁷ respectively.



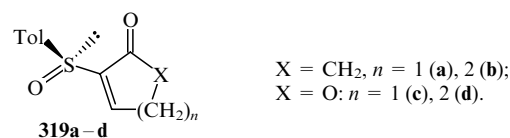
α -Silylated vinylsulfonyl groups at C(6) of the pyran ring were used for 'pseudoeantiomeric' addition.²⁹⁵ In the total synthesis of tautomycin (**316**), compounds **317** and **318** were employed for the spiro-fusion of rings pseudoeantiomeric with respect to okadaic acid as well as for the introduction of the methyl group at position 3 of the segment *C*. The segments *C* and *B* were coupled



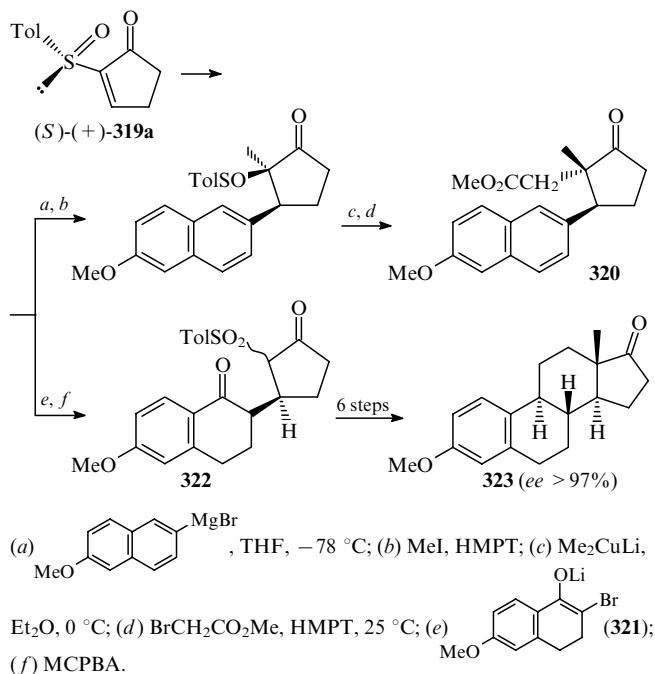
R = SiMe₂Bu^t.

by the reaction of the C(16)-sulfonyl carbanion of the former with the C(17),C(18)-epoxide of the latter in the presence of BF₃·Et₂O. Esterification with the segment *A* completed the synthesis.^{296, 297}

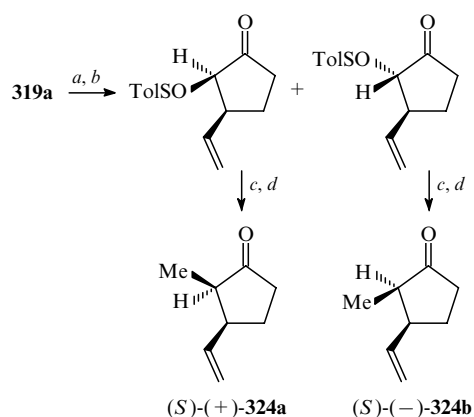
Studies by Posner *et al.*^{11, 298} have played a decisive role in the development of asymmetric synthesis based on reactions of C-nucleophiles with enantiomerically pure vinyl sulfoxides. These reactions made use of enantiomerically pure 2-(sulfinyl)-cycloalkenones **319a,b** or 2-(sulfinyl)alkenolides **319c,d** as the substrates. Convenient procedures for the synthesis of these compounds were devised. The carbonyl group activates the double bond thus promoting Michael-type addition of C-nucleophiles. The stereochemistry of addition can be controlled by adding chelating agents. Thus conditions for the *Si*-attack of the nucleophile are created in the presence of ZnBr₂, which binds the sulfinyl and carbonyl groups to form a rigid chelate. In the absence of this additive, *Re*-attack predominantly occurs.



Posner and coworkers used not only organometallic compounds but also lithium enolates as nucleophiles. The high optical purity of the resulting compounds was attained by varying the reaction parameters and using enantiomerically pure precursors. Thus the formal synthesis of the methyl ether of (*S,S*)-11-oxoequilenin was carried out starting from (*S*)-(+)-2-(tolylsulfinyl)cyclopent-2-enone [(*S*)-(+)-**319a**] via the secosteroid **320**.^{299, 300} The reaction of the same vinyl sulfone **319a** with lithium enolate **321** gave rise to the Michael addition product **322** with a diastereoselectivity of 91%–94%. The latter compound was converted in six steps into methyl ether of estradiol (**323**) with *ee* > 97%.³⁰¹

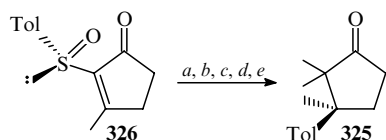


Vinylation of vinyl sulfone **319a** in the presence of ZnBr₂ followed by methylation afforded a mixture of diastereomers of trisubstituted cyclopentanones. Reductive desulfinylation of the latter made it possible to obtain enantiomerically pure substituted cyclopentanones **324a,b**, which are required for the synthesis of steroids.³⁰²



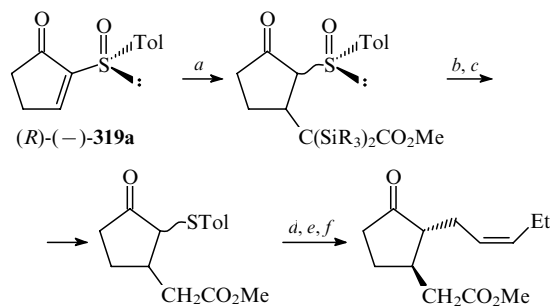
(a) ZnBr₂; (b) CH₂=CHMgBr; (c) MeI; (d) Al/Hg.

Quaternary chiral centres can be generated using 3-alkyl-substituted tolylsulfonylcyclopentenone as the starting compound.³⁰³ For example, vinyl sulfone **326** was used in the stereoconvergent synthesis of the sesquiterpene (+)- α -cuparenone (**325**); however, the *ee* value of the resulting product was only 70%.



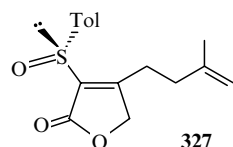
(a) Tol₂CuLi; (b) MCPBA; (c) Bu^tOK; (d) MeI; (e) Me₂CuLi, MeI.

The five-step synthesis of enantiomerically pure (–)-methyl jasmonate with *ee* > 98% was carried out³⁰⁴ starting from vinyl sulfone (R)-(–)-**319a**.



(a) (R₃Si)₂C(Li)CO₂Me; (b) P₂I₄; (c) KF; (d) NaH; (e) BrCH₂Et; (f) Ra/Ni.

Using enantiomerically pure (S)-(+)-tolylsulfinylbutenolide **319c**³⁰⁵ or -pentenolide **319d**³⁰⁶ as the starting compounds in the reactions with a Grignard reagent in the presence of ZnBr₂ or with substituted lithium enolates, enantiomerically pure antitumour (–)-podarhizon and 3-substituted esters of glutaric acids, respectively, were prepared. Holton *et al.*³⁰⁷ used an analogous reaction and vinyl sulfoxide **327** as the starting compound in the formal total synthesis of aphidicolin, which exhibits *in vitro* activity against the virus *Herpes simplex*.

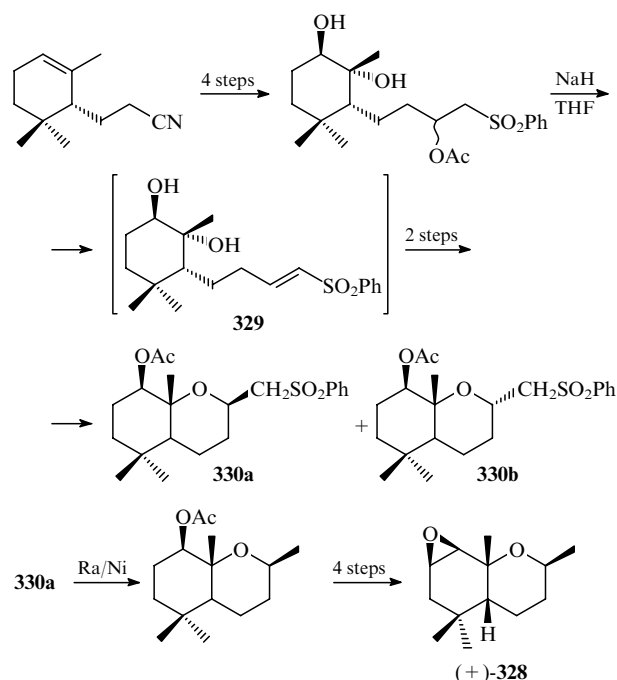


b. Addition of heteronucleophiles

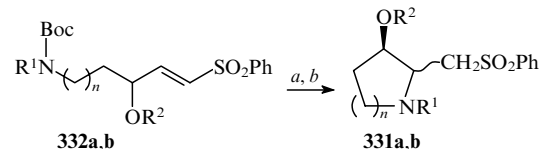
In the synthesis of natural products, reactions of vinyl sulfones or vinyl sulfoxides with alkoxides or amines resulting in the construction of C–O or C–N bonds were used almost exclusively in

the intramolecular versions regardless of the nature of the acceptor.

Thus the key step of the 15-step enantioselective total synthesis of the pheromone (1*R*,3*S*,6*R*,9*S*,10*S*)-9,10-epoxytetrahydroedulan (+)-**328** involved cyclisation of hydroxyvinyl sulfone **329** yielding compounds **330a,b** in a ratio of 3.5:1.³⁰⁸

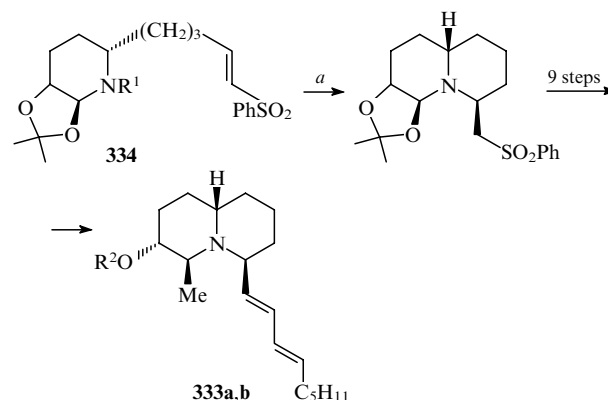


In the synthesis³⁰⁹ of 2,3-disubstituted pyrrolidines **331a** and piperidines **331b** (the starting materials in the synthesis of biologically active compounds) from acyclic alkoxy- and hydroxy-substituted aminovinyl sulfones **332a,b**, cyclisation proceeded also nonstereoselectively. The best *cis*-stereoselectivity (~80%) was achieved with the use of the hydroxy derivatives **332a**. The protection of the hydroxy group (the best results were obtained with R³ = PrⁱSi) favours *trans*-stereoselectivity.



n = 1 (**331a**), 2 (**331b**); R¹ = H, (CH₂)₂CO₂Me; R² = H (**332a**), PrⁱSi (**332b**); (a) CF₃CO₂H, CH₂Cl₂; (b) Et₂NH, THF, –78 °C.

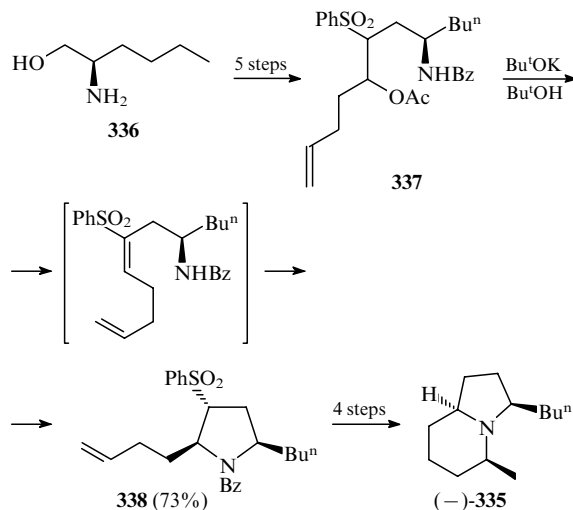
In more rigid systems, for example, in the synthesis of the alkaloids clavicipines A and B **333a,b** from monocyclic com-



R¹ = Troc (trityloxycarbonyl); R² = Ac (**a**), H (**b**); (a) 10% C/Pd, THF, NH₄OAc, 20 °C, 48 h (94%).

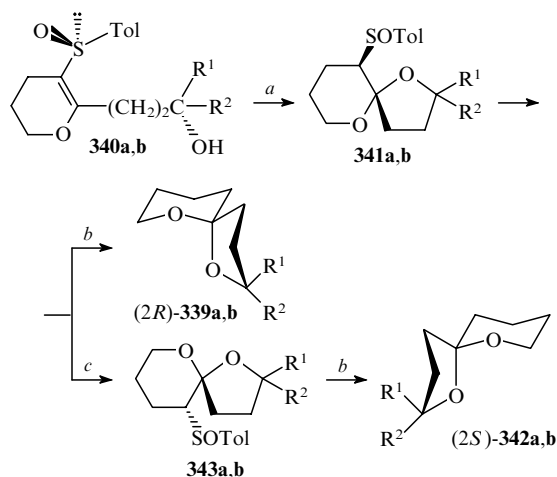
pound **334**, cyclisation through β -amination of the double bond of the vinylsulfone fragment occurs with a high stereoselectivity.³¹⁰

In the synthesis of (–)-monomorine **335**, 5-*endo-trig* cyclisation of compound **337** prepared from norleucinol **336** took place also in a highly stereoselective manner.³¹¹ The construction of the second ring from the monocyclic intermediate **338** occurred through intramolecular reductive amination.



Intramolecular addition of heteronucleophiles at the C=C bonds of vinyl sulfoxides plays a considerable role in the asymmetric synthesis.¹²

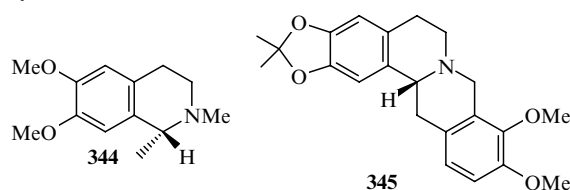
In the series of studies performed by Iwata *et al.*,^{312–315} the addition of remote hydroxy groups to the vinyl sulfoxide fragment was used for the construction of enantiomerically pure dioxaspirodecans and -undecanes, which are the major components of pheromones of many insects. The enantioselectivity of spirocyclisation is achieved owing to the asymmetric induction of the chiral sulfinyl group due to which this method has advantages over some others.^{100, 101} Dioxaspirodecans (2*R*)-**339a,b**, which are pheromones of the wasp *Paravespula vulgaris*,^{312, 313} were prepared by the action of KH on 5-hydroxydihydropyran sulfoxides **340a,b** followed by reductive desulfination of the reaction products **341a,b**. Two other diastereomers of the pheromone, *viz.*, **342a,b**, were synthesised by isomerisation of the cyclisation product in an acidic medium followed by reductive desulfination of isomeric sulfoxides **343a,b**. The closure of the six-membered rings by an analogous intramolecular reaction afforded (*R*)- and (*S*)-1,7-dioxaspiro[5.5]undecanes **61**^{313, 314} and more complex molecules of talaromycins A and B, which are metabolites of the toxic mushroom *Talaromyces stipitatus*.³¹⁵



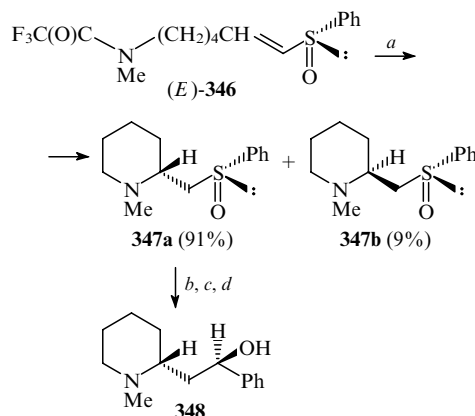
$R^1 = \text{H}$, $R^2 = \text{Me}$ (a); $R^1 = \text{Me}$, $R^2 = \text{H}$ (b); (a) KH, THF, -78°C ; (b) Ra/Ni, MeOH; (c) TsOH.

Solladie *et al.*¹⁶⁸ used cyclisation involving a remote hydroxy group and the C=C bond of the chiral vinylsulfinyl fragment of the molecule as one of the steps in the above-considered synthesis of a vitamin E precursor, *viz.*, (+)-(*S*)-**122**.

Polycyclic alkaloids, such as (+)-carnegine (**344**) and (+)-canadine (**345**), can be prepared by intramolecular amination of vinylsulfinyl bonds in spite of the fact that this process is not always stereoselective.^{316, 317}

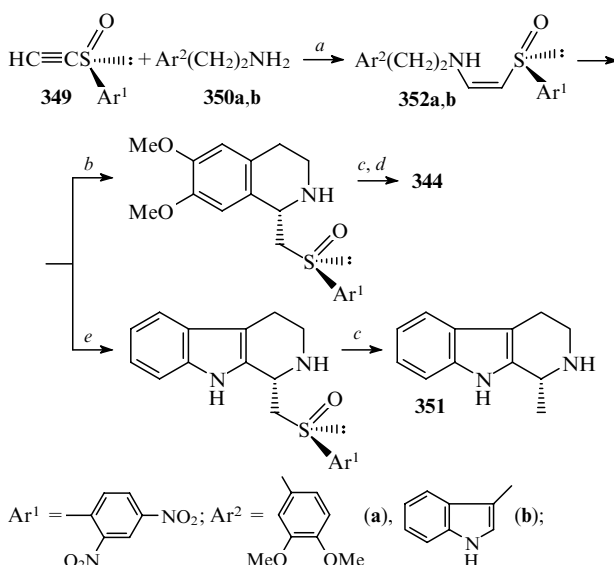


Monocyclic (+)- and (–)-sedamines were synthesised³¹⁶ from linear precursors, *viz.*, substituted (*E*)- and (*Z*)-alkenyl sulfoxides. Thus cyclisation of the sulfoxide (*E*)-**346** followed by chain elongation in the reaction of the α -sulfinyl carbanion of diastereomer **347a** with benzaldehyde and reductive desulfinylation of the reaction product afforded (+)-sedamine (**348**). (–)-Sedamine was prepared according to the same procedure starting from the (*Z*)-isomer of the sulfoxide **346**.



(a) $\text{PhCH}_2\text{NEt}_3\text{OH}$, -40°C ; (b) LDA; (c) PhCHO; (d) Ra/Ni.

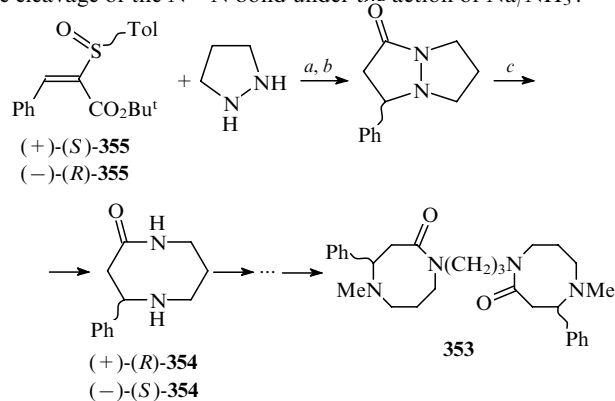
An alternative procedure for the preparation of carnegine (**344**) was developed³¹⁸ based on the reaction of enantiomerically pure (*R*)-2,4-dinitrophenylethynyl sulfoxide (**349**) containing the highly electrophilic triple bond with 2-(3,4-dimethoxyphenyl)-



(a) 20°C ; (b) **350a**, $\text{CF}_3\text{CO}_2\text{H}$, 0°C , 100%; (c) Ra/Ni; (d) CH_2O , NaCNBH_3 ; (e) **350b**, TsOH, MeOH, -30°C (70%).

ethylamine (**350a**). The tricyclic alkaloid (+)-tetrahydroharman (**351**) was prepared with a rather high selectivity starting from amine **350b** containing the indole substituent *via* the vinyl sulfoxide **352b**.

Intermolecular addition of a nitrogen nucleophile to the vinylsulfinyl bond was used in the synthesis of structurally unique (*R,R*)- and (*S,S*)-homalines **353** from epimeric 4-phenyl-1,5-diazacyclooctan-2-ones [(*R*)-(+)-**354**] and (*S*)-(–)-**354**.³¹⁹ The reaction of pyrazolidine with enantiomerically pure substituted (*R*)- or (*S*)-(*E*)-vinyl sulfoxides **355** in an excess of Bu^tOK followed by the removal of the sulfinyl group under the action of SmI₂ afforded bicyclic compounds. The target products were prepared from these bicyclic compound in two steps after reductive cleavage of the N–N bond under the action of Na/NH₃.

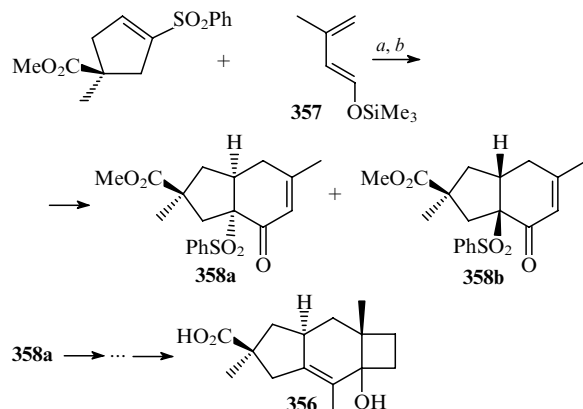


(a) Bu^tOK; (b) SmI₂; (c) Na/NH₃.

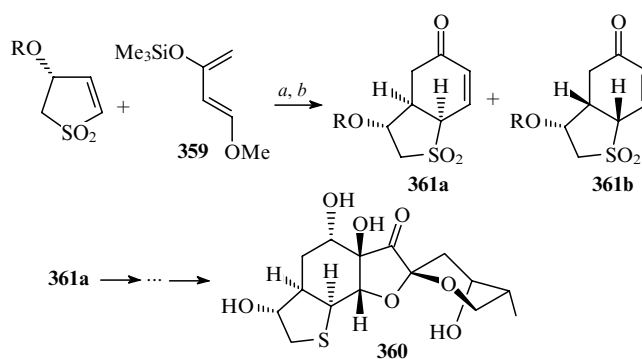
2. The Diels–Alder reaction

a. Sulfonyl- and sulfinyl-containing dienophiles

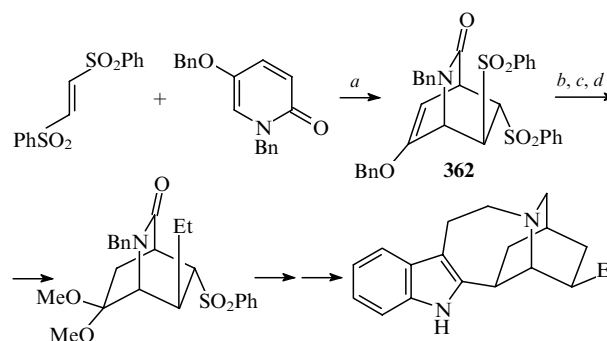
The high reactivity of vinyl sulfones as dienophiles in [4 + 2] cycloaddition reactions was reported in the 1960s. Ethyl vinyl sulfone readily enters into Diels–Alder reactions not only with electron-rich dienes (the reaction with cyclopentadiene is exothermic), but also with electron-deficient dienes (for example, with hexachlorocyclopentadiene³²⁰). More recently, owing to the fact that the adducts of vinyl sulfones can readily undergo reductive desulfonation, the latter have found application as equivalents of nonactivated alkenes and alkynes, which are difficult to introduce into the [4 + 2] cycloaddition reactions.^{321, 322} However, the Diels–Alder reactions are rather rarely used for the preparation of biologically active compounds due apparently to their low stereoselectivity. The first step of the synthesis of sesquiterpenoid sterpuric acid (**356**) involved cycloaddition of cyclic vinyl sulfone to the highly electrophilic Danishefsky diene (**357**).^{323, 324} The ratio between the target isomer **358a** and the undesirable isomer **358b** was ~ 2 : 1 (the total yield of the final product was 11%). The reaction of 3-silyloxy-2-sulfolene with diene **359**, which is the key



(a) ~ 150 °C, 5 days; (b) oxidation.



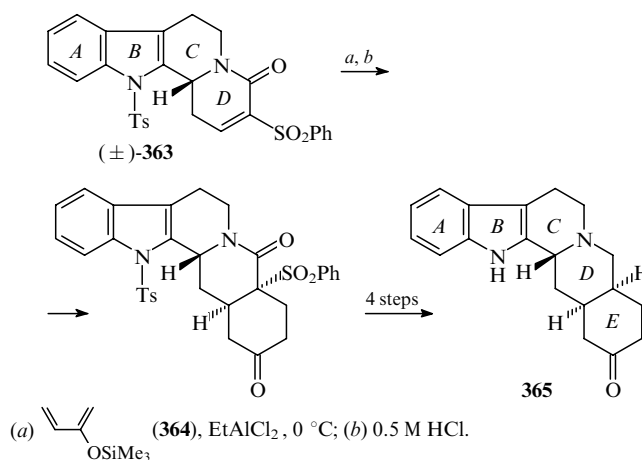
R = Pr₃Si; (a) 170–180 °C, 48 h; (b) Py·TsOH, Δ (82%–85%).



(a) 150 °C, 8 days; (b) 2 M HCl, (MeO)₃CH; (c) KOH, THF; (d) EtCuMgI.

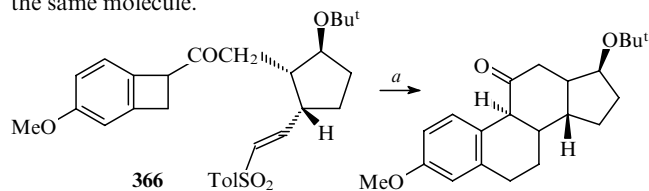
step in the formal synthesis of breynolide (**360**), also proceeded nonselectively to form a mixture of adducts **361a,b**.³²⁵ (*E*)-1,2-Bis(diphenylsulfonyl)ethene is a more efficient dienophile. Its reaction with 5-benzoyloxy-2-pyridone proceeded with a higher selectivity and was used in the synthesis of racemic ibogamine *via* the adduct **362** (the total yield was 14%).^{326, 327}

In the absence of catalysts, [4 + 2] cycloaddition involving vinyl sulfones proceeds at rather high temperature. The use of catalysts makes it possible to use milder reaction conditions and to enhance the selectivity. Thus the selectivity of the Diels–Alder reaction of tetracyclic vinyl sulfone **363** with diene **364** in the presence of EtAlCl₂ at 0 °C was higher than 90%. Such strategy for the ring buildup made it possible to perform the C(15)- and C(20)-enantioselective synthesis of racemic alkaloid 3-*epi*-allo-yohimbone (**365**) with a skeleton similar to that of reserpine.³²⁸



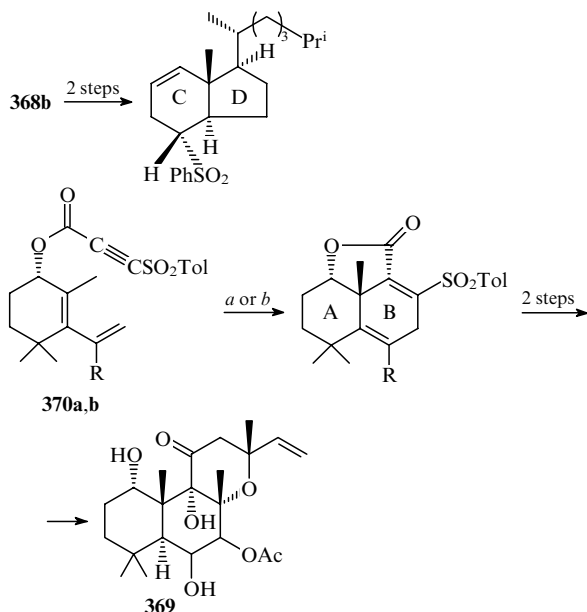
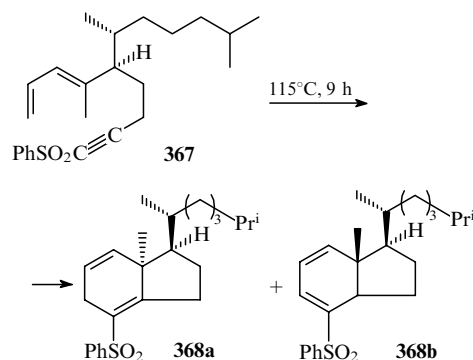
An application of intramolecular [4 + 2] cycloaddition involving α,β-unsaturated sulfonyl fragments has been described. Thus the stereospecific construction of the skeleton of *cis-anti-cis*-estrone was carried out³²⁹ by the reaction of the *o*-quinodimethane fragment formed upon pyrolysis of the benzocyclo-

butane moiety of compound **366** with the vinylsulfonyl group of the same molecule.

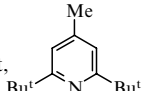


(a) 195 °C, 1,2-Cl₂C₆H₄, 6 h (~62%).

Based on their experience on intramolecular Diels–Alder reactions of polyene sulfones,³³⁰ Craig *et al.*³³¹ attempted to use this approach in the synthesis of vitamin D₃ and its analogues, which have attracted growing interest because of the discovery of new pharmacological properties of these compounds.³³² However, the construction of the block CD for the synthesis of vitamin D₃ can be performed³³³ only starting from compound **367** containing the highly reactive sulfonylethynyl fragment. Selective hydrogenation of one of the C=C bonds in the major reaction product **368b** afforded the key intermediate in the synthesis of vitamin D₃, *viz.*, sulfone containing the rings CD. Corey *et al.*^{334–336} used ethynylsulfonyl precursors for the construction of the rings AB of forskolin (**369**) possessing valuable pharmacological properties. Owing to the additional activation of the triple bonds in compounds **370a,b** with ester groups, cyclisation



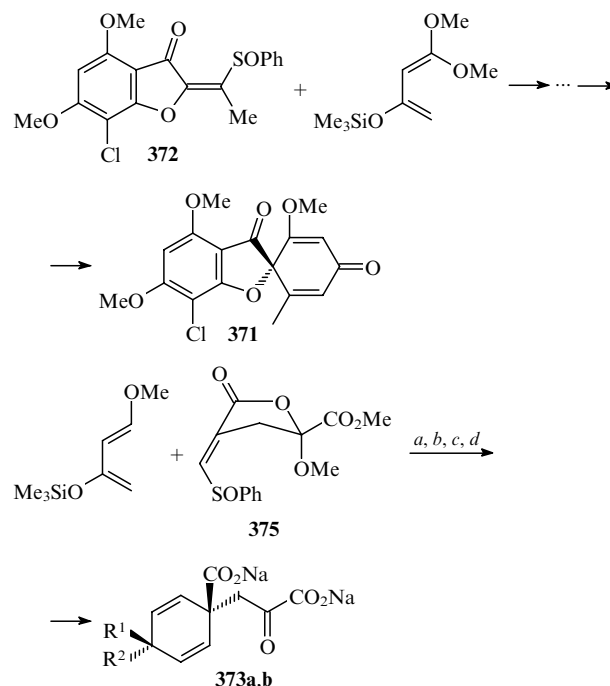
R = H (a), OCO₂Et (b); (a) R = H, CH₂Cl₂, 23 °C, 36 h (64%, *ee* 97%);

(b) R = OCO₂Et, , 95 °C, 48 h (65%, *ee* 93%).

occurred in the absence of a catalyst under mild conditions with a high enantioselectivity.

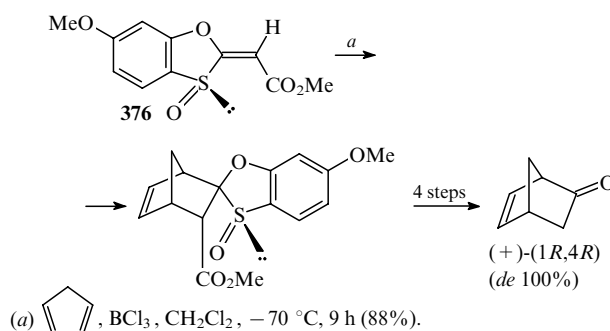
The introduction of activating groups and the addition of catalysts, which allow one to perform the Diels–Alder reactions under milder conditions, are particularly necessary if less reactive vinyl sulfoxides are used as dienophiles.

The Diels–Alder synthesis involving polyfunctional racemic vinyl sulfoxides was applied, for example, in the preparation of (±)-dehydrogriseofulvin (**371**)³³⁷ starting from the sulfoxide **372** or sodium salts of prephenates **373** *via* the intermediates **374a,b**, which were generated from the sulfoxide **375**.³³⁸ When surveying his investigations, Danishefsky particularly emphasised these studies.³³⁹ The reactions of vinyl sulfoxides even with Danishefsky's silyloxydienes necessitated prolonged heating and were accompanied by elimination of sulfenic acid.



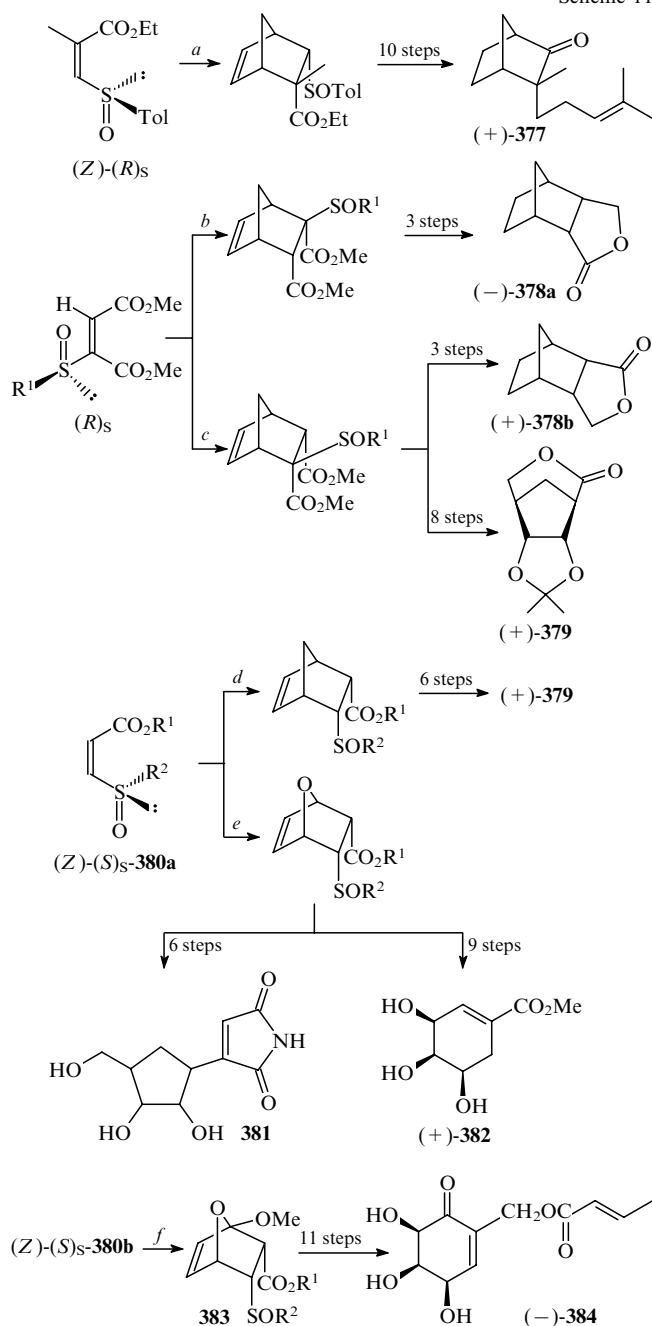
R¹ = OH, R² = H (a); R¹ = H, R² = OH (b); (a) 100 °C, 20 h; (b) AcOH, AcOEt; (c) BBN (9-borabicyclononane); (d) NaOH.

The development of procedures for efficient asymmetric synthesis starting from enantiomerically pure sulfinyl-containing dienophiles presented the major problem. The search for the optimum reaction conditions and for the chiral sulfinyl dienophile of choice for the synthesis of (+)-(1*R*,4*R*)- and (–)-(1*S*,4*S*)-enantiomers of norborn-4-enone was carried out using the [4 + 2] cycloaddition of cyclopentadiene to (+)-(*R*)-tolyl vinyl sulfoxide³⁴⁰ and its analogues^{341,342} as examples. The full selectivity was achieved only with the use of a more complex compound, *viz.*, a ketene equivalent **376**. The reaction of the latter with cyclopentadiene in the presence of BCl₃ at –70 °C gave only one adduct, which was transformed into (+)-(1*R*,4*R*)-norborn-4-enone.³⁴³ The reaction proceeded selectively due to the formation



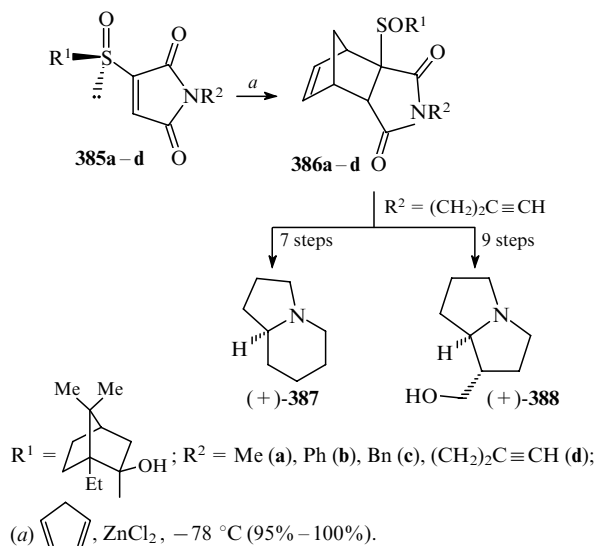
The synthesis of (+)-*epi*- β -santalene **377** involved the reaction of cyclopentadiene with ethyl (*Z*)-(*R*)_S-2-methyl-3-(tolylsulfinyl)-prop-2-enoate (Scheme 11).^{344,345} In this synthesis, the reaction

Scheme 11

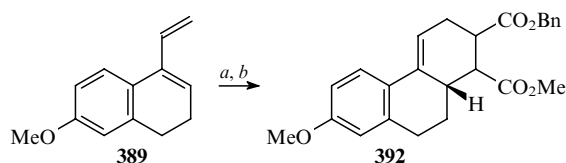


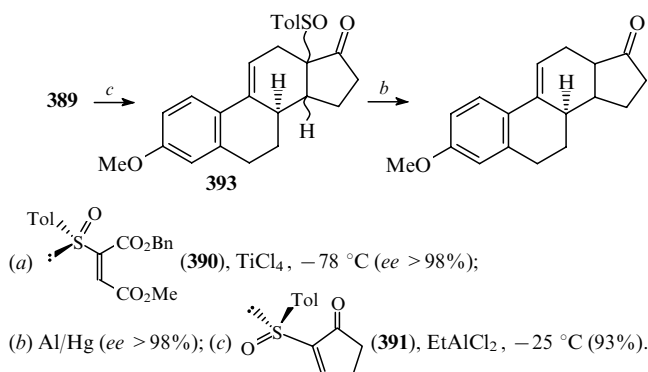
R¹ = menthyl; R² = 2-pyridyl (**380a**), R² = 3-trifluoromethyl-2-pyridyl (**380b**); (a) , 90 °C, 6 h (87%); (b) , 25 °C, 19 h (87%); (c) , ZnCl₂, -20 °C, 3.5 h (94%); (d) , Et₂AlCl, -78 °C (94%); (e) , Et₂AlCl, -78 °C (~70%); (f) , 0 °C, 6 days (~100%).

Chiral *N*-substituted sulfinylmaleimides **385a–d** are efficient dienophiles. These compounds react with cyclopentadiene in the presence of ZnCl_2 at low temperature to form almost exclusively *exo*-adducts **386a–d** in quantitative yields.³⁵² The adduct **386d** was used³⁵³ for the preparation of the bicyclic alkaloids (+)-indolizidine **387** and (+)-laburnine **388**.



The search for new types of electron-rich dienes holds promise. This will extend the scope of synthetic applications of sulfinyl-containing dienophiles. For example, condensation of 'Dane's diene' (**389**) with the sulfinyl-substituted ester of maleic acid **390**³⁵⁴ or with sulfinyl-substituted cyclopentenone **391**³⁵⁵ afforded the adducts **392** and **393**, respectively, which are precursors in the steroid synthesis, with a high diastereoselectivity.





The reaction of the diene **389** with the sulfoxide **390** was accompanied by spontaneous elimination of sulfenic acid.

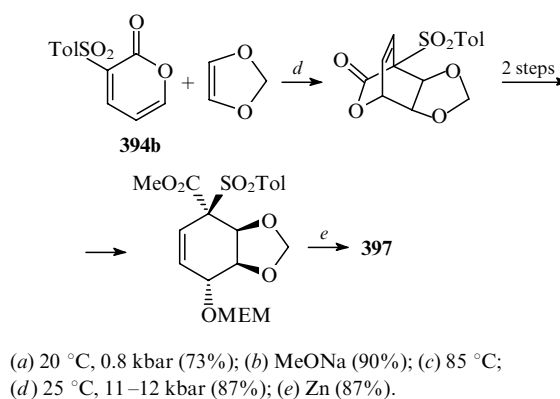
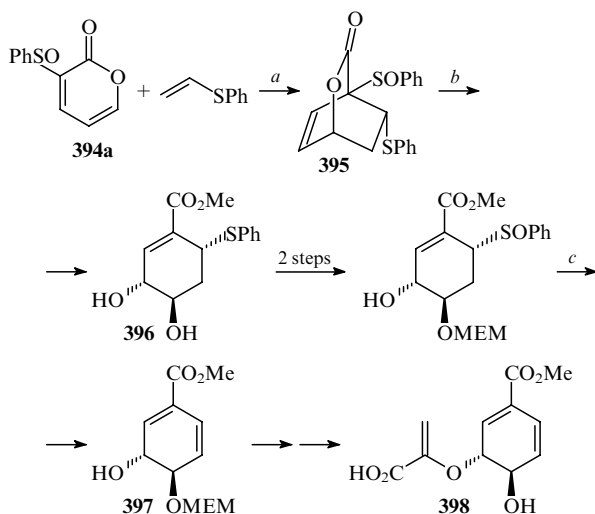
b. Sulfonyl- and sulfinyl-containing dienes

As yet, sulfonyl-substituted and, particularly, enantiomerically pure sulfinyl-substituted dienes have received little use in the synthesis of natural products.

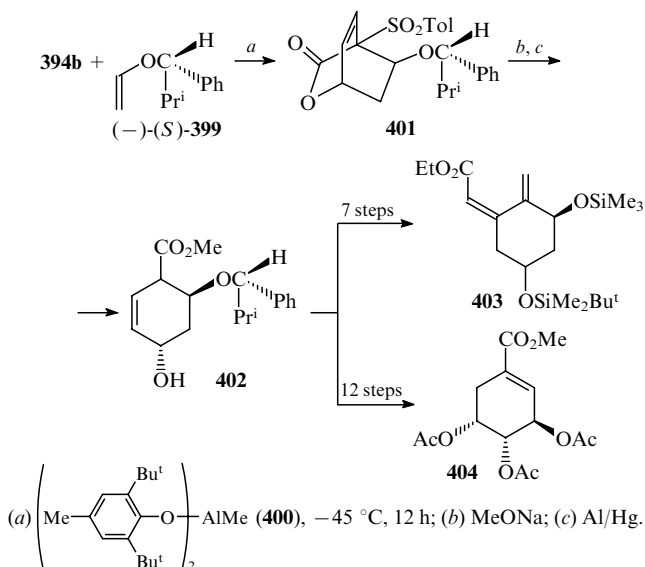
Evans³⁵⁶ was the first to propose a tandem $[4 + 2]$ cycloaddition of a racemic sulfinyl-containing diene and the sulfonyl-sulfenate rearrangement of the adduct using the synthesis of a derivative of the hasubanan series as an example.

More recently, Posner and coworkers (see the review³⁵⁷) performed systematic studies of the Diels–Alder reactions of 3-sulfinyl- (**394a**) and 3-sulfonyl-2-pyrones (**394b**) with electron-rich dienophiles, such as vinyl ethers or vinyl sulfides. Unlike other substituted pyrones whose Diels–Alder reactions proceed only at high temperatures (resulting in the degradation of the initially formed adducts), the pyrones **394a,b** at low temperatures (sometimes at high pressure) give polysubstituted bicyclic lactones, which are excellent starting compounds for the preparation of various natural products.

Thus the reaction of the sulfinyl-substituted pyrone **394a** with ethyl vinyl sulfide proceeded stereoselectively to form³⁵⁸ the *endo*-adduct **395**, which was converted into tetrasubstituted cyclohexene **396** through the sulfoxide-sulfenate rearrangement under conditions of alkaline methanolysis. Subsequent transformations afforded substituted cyclohexadiene **397**, which is the key intermediate in the synthesis of ($\pm$)-chorismic acid (**398**). A shorter synthetic path for the cyclohexadiene **397** is based on the reaction of sulfonylpyrone **394b** with 1,3-dioxole.³⁵⁹

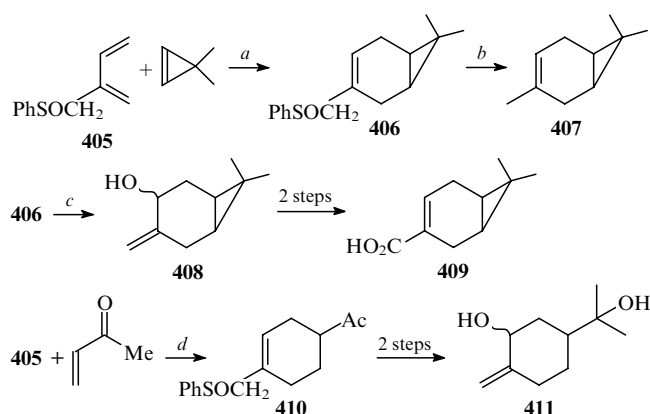


Posner and coworkers performed asymmetric syntheses of a number of enantiomerically pure natural compounds by introducing sulfonylpyrone **394b** into the Diels–Alder reaction with optically pure vinyl ether (–)-(*S*)-**399**^{360–362} catalysed by Lewis acid **400**.³⁶⁰ The transformation of the *endo*-adduct **401**, which was obtained with a high stereoselectivity, afforded trisubstituted cyclohexene (–)-**402**. A somewhat lower stereoselectivity was achieved when this reaction was carried out in the absence of a catalyst at $25\text{ }^\circ\text{C}$.³⁶¹ The cyclohexene **402** served as the starting compound for the preparation of the key intermediate **403** (the total yield was 62%) in the total synthesis of $1\alpha,25\alpha$ -dihydroxyvitamin D_3 as well as for the synthesis of methyl (–)-tri-*O*-acetyl-4-*epi*-shikimate (**404**) (the total yield was 23.4%, $ee > 98\%$).



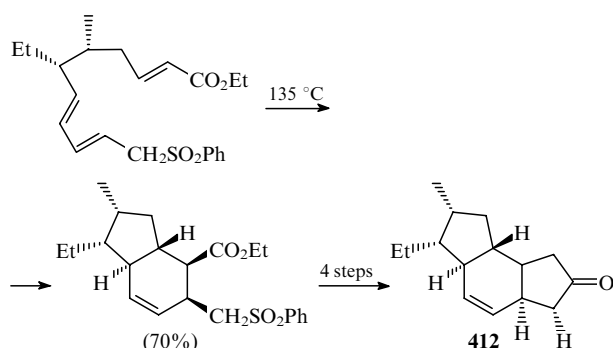
Readily available racemic 2-(phenylsulfinylmethyl)buta-1,3-diene (**405**) is an active diene.³⁶³ This compound reacted with dimethylcyclopropane to give a mixture of *exo*- and *endo*-adducts **406**. After reductive desulfonylation, the *exo*-adduct was converted into Δ^3 -carene (**407**). The sulfoxide-sulfenate rearrangement of compound **406** under the action of $\text{P}(\text{OEt})_3$ afforded the hydroxy derivative **408** from which racemic chaminic acid (**409**) was prepared. Thermal condensation of the diene **405** with methyl vinyl ketone gave rise to a mixture of 1,4- and 1,3-substituted cyclohexenes in a ratio of 3 : 1. The adduct **410** was converted into racemic $\Delta^{1(7)}$ -menthene-2,8-diol (**411**) in three steps.

Sulfonyl- and sulfinyl-substituted diene units can be involved in intramolecular $[4 + 2]$ cycloaddition. For example, this procedure was used for the preparation of compound **412**, which is an

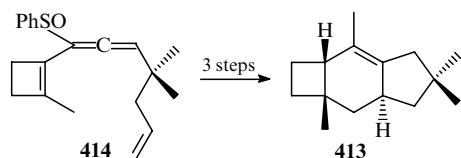


(a) 80 °C, 5 kbar; (b) Li, NH₃ (liquid); (c) P(OEt)₃; (d) PhH, 80 °C.

important fragment in the total synthesis of the macrolide ikarugamycin.³⁶⁴

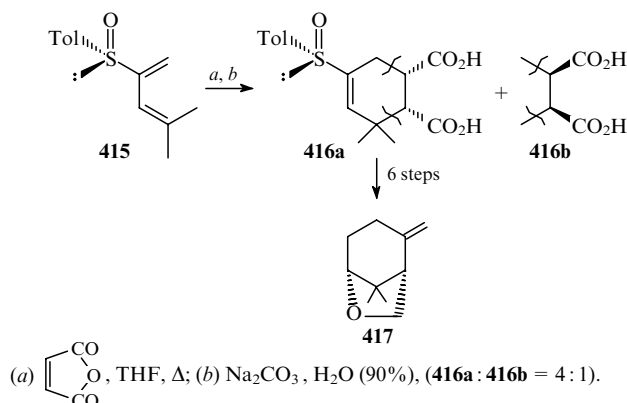


A short synthesis of sesquiterpenoid (+)-sterpurene (**413**) was carried out³⁶⁵ using the cascade intramolecular [4 + 2] cycloaddition involving the diene system of sulfinyl-substituted tetraene **414**.



Convenient procedures for the preparation of enantiomerically pure 2-sulfinyl-substituted butadienes have been developed recently.^{366, 367} The transformation of the *endo*-adduct (**416a**) of diene **415** with maleic anhydride in the synthesis of monoterpenoid (–)-(1*S*,5*R*)-karahana ether (**417**) (*ee* > 93%) is the first

example of an asymmetric synthesis of a natural product with the use of such dienes.³⁶⁸



(a) $\begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{O} \end{array}$, THF, Δ ; (b) Na₂CO₃, H₂O (90%), (**416a** : **416b** = 4 : 1).

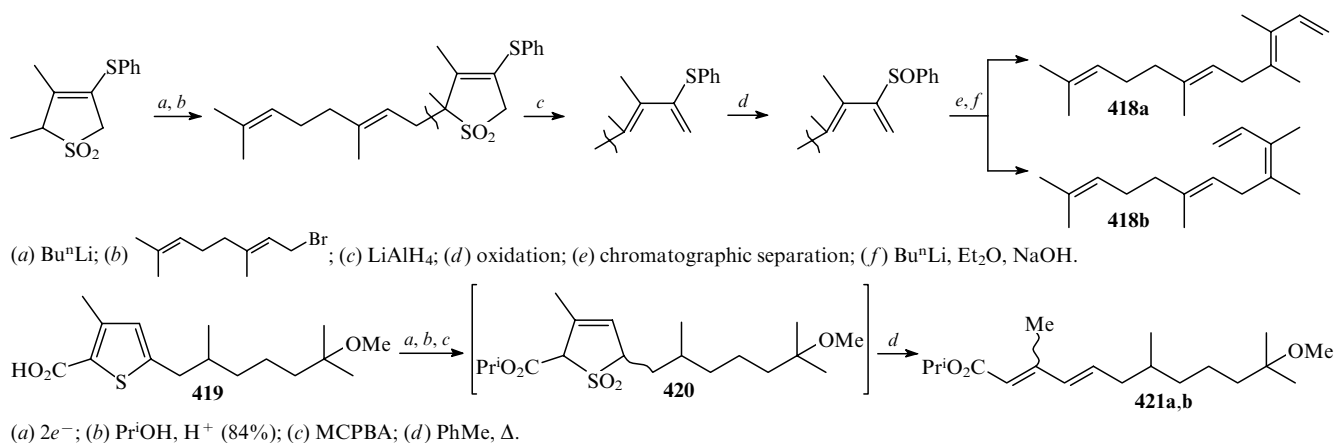
3. Syntheses based on elimination of SO₂ from 2,5-dihydrothiophene 1,1-dioxides (3-sulfolenes)

3-Sulfolenes readily eliminate SO₂ to form substituted buta-1,3-dienes. This process is the cheletropic ring-opening reaction which obeys the Woodward–Hoffmann rule and occurs under conditions of pyrolysis, sometimes in the presence of bases. The introduction of substituents into the sulfolene ring, which can be readily performed, for example, by alkylation at the α -position, followed by thermolysis allows one to prepare various buta-1,3-dienes starting from 3-sulfolenes. These butadienes can be used in the synthesis of polyunsaturated linear and carbocyclic natural compounds. Thus the homofarnesene components of the fire-ant trail pheromone **418a,b** were prepared³⁶⁹ from 2,3-dimethyl-4-(phenylthio)-3-sulfolene (Scheme 12). Polysubstituted thiophene **419** was converted into 3-sulfolene **420** by electrolytic reduction followed by oxidation at the sulfur atom.³⁷⁰ The compound **420** was subjected to *in situ* thermolysis resulting in a mixture of a juvenoid methoprene **421** and its (2*Z*,4*E*)-isomer.

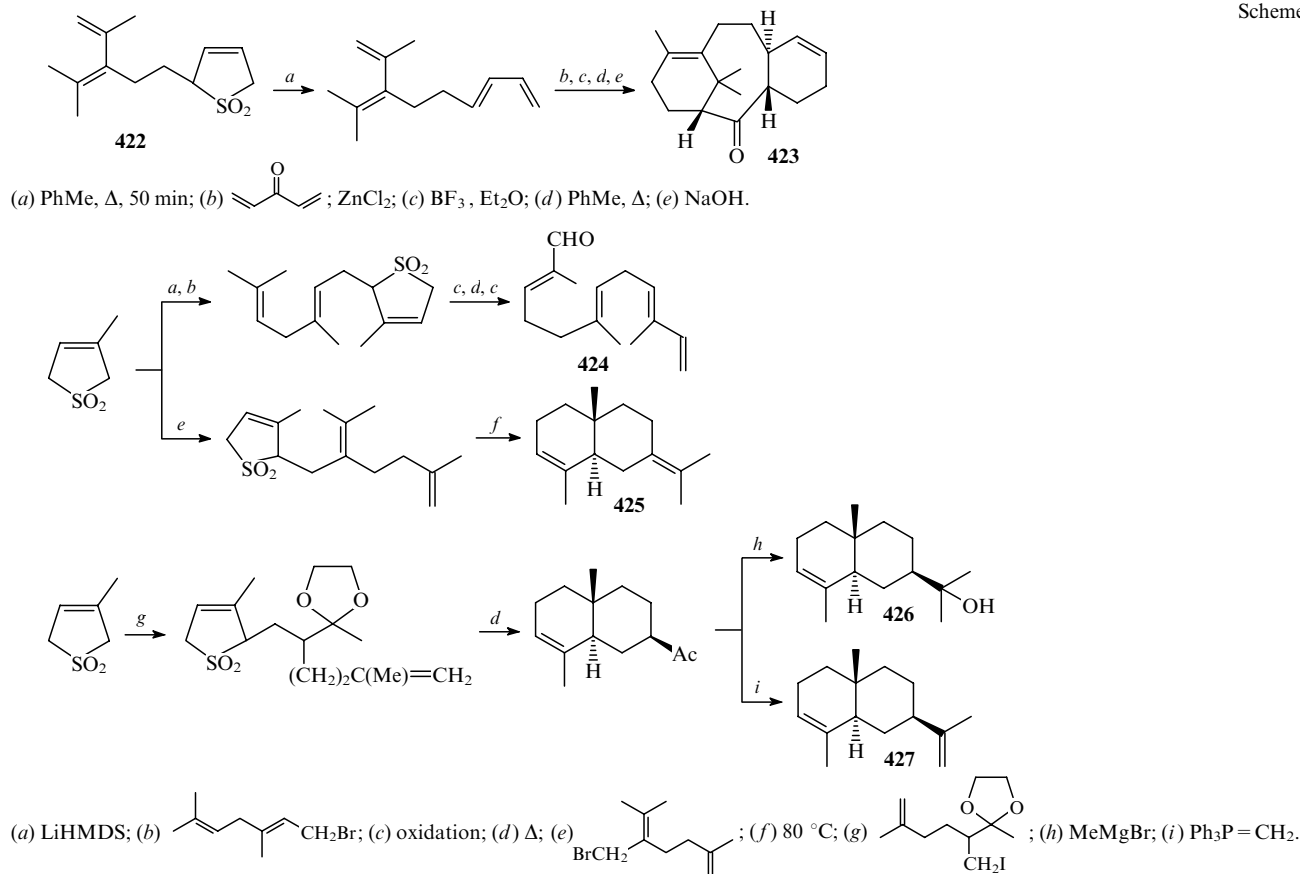
Sulfolene **422** was used as the starting material³⁷¹ for the preparation of tricyclic compound **423** containing the taxane ring system. 3-Methyl-3-sulfolene served as the starting compound in many syntheses of natural compounds, for example, of open-chain α -sinensal (**424**) (an important contributor to the odour of the Chinese orange oil)³⁷² or bicyclic terpenoids of the eudesmane series **425–427**.³⁷³ In the latter cases, the intramolecular Diels–Alder reactions proceeded with extremely high stereoselectivities (Scheme 13).

The use of nitrogen-containing dienophilic groups (for example, imine or enamide groups) in the intramolecular Diels–Alder reactions opens up the way to the construction of racemic alkaloids (Scheme 14). Apparently, the first to be performed was the short synthesis of racemic elaeokanine A (**289a**) *via* the

Scheme 12



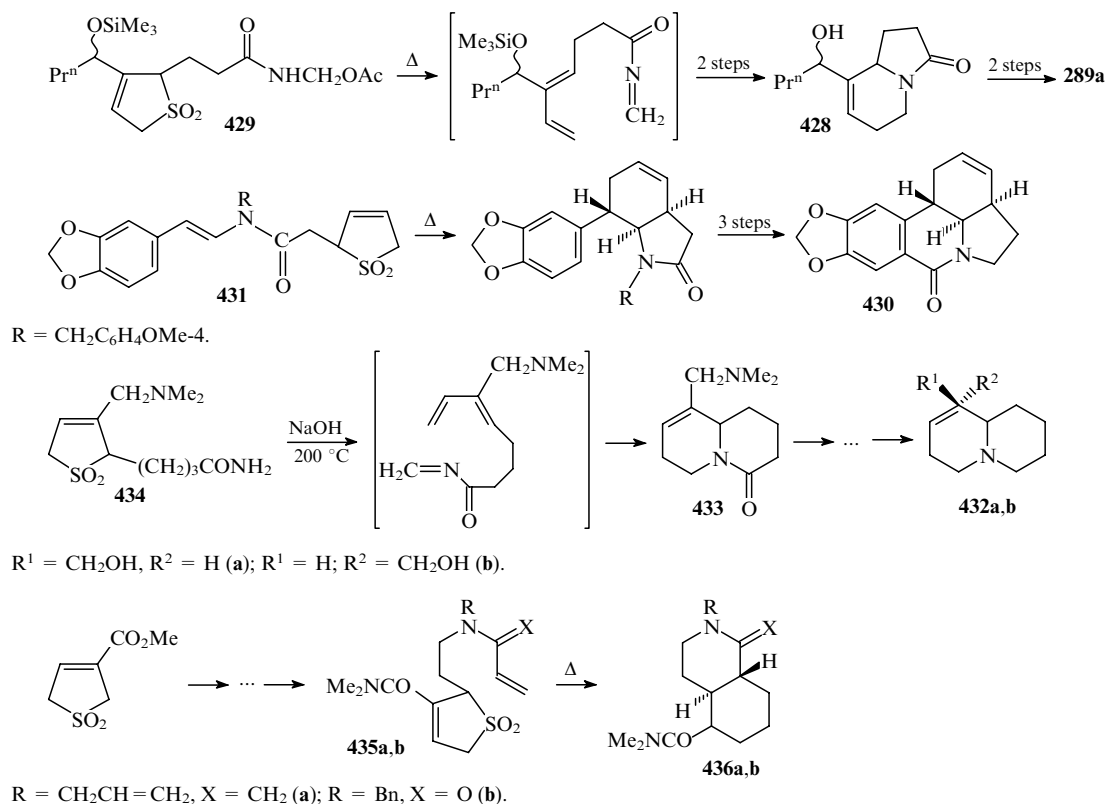
Scheme 13



intermediate **428** starting from the sulfolene **429**.³⁷⁴ Elimination of SO₂ and cyclisation were carried out by passing compound **429** through a heated column (370–390 °C) filled with glass helices. Martin *et al.*³⁷⁵ performed the formal total synthesis of pentacyclic lycorine (a natural plant-growth inhibitor, which is an important alkaloid of the *Amaryllidaceae* family) via the key

precursor lycorane **430**. Sulfolene-containing enamide **431** was used as the starting compound. Short syntheses of racemic lupinine **432a** and epilupinine **432b** were performed starting from bicyclic compound **433**, which has been prepared by pyrolysis and the intramolecular Diels–Alder reaction of disubstituted sulfolene **434**.³⁷⁶ Analogous conversions of the precursors **435a,b**,

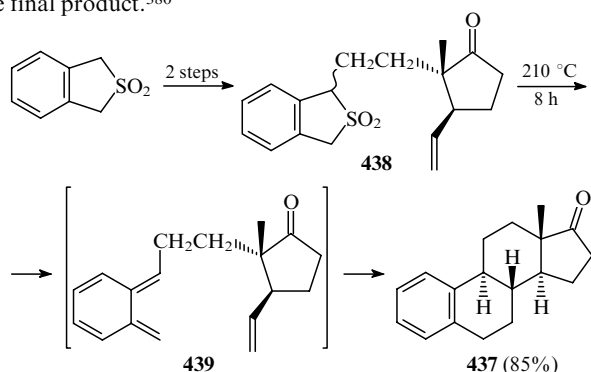
Scheme 14



which have been prepared from 3-methoxycarbonyl-3-sulfolene, afforded the bicyclic systems **436a,b**. The latter served as the starting compounds in the synthesis of heteroyohimboids.³⁷⁷

The sulfolene grouping has also been used as a protective group in modifications of vitamin D₃. For the purpose of introducing methyl groups at C(6) and C(19)³⁷⁸ or the fluorine atom at C(19),³⁷⁹ an adduct of vitamin D₃ with SO₂ at its 1,3-diene fragment has been initially prepared. After completion of the required transformations, the adduct was decomposed by mild thermolysis.

In the total synthesis of racemic estra-1,3,5(10)-trien-17-one (**437**), a mixture of epimers of substituted 1,3-dihydrobenzo[*c*]-thiophene 2,2-dioxide **438** was used as the precursor. This mixture gave rise to the quinodimethane intermediate **439** upon thermal elimination of SO₂, which underwent stereospecific cyclisation to the final product.³⁸⁰



VI. Conclusion

Among reactions of sulfoxides and sulfones playing an important role in the synthesis of natural compounds, alkylation of carbanions obtained from these compounds or the Julia olefination became conventional processes. However, the improvement of these procedures is still in progress. Thus the use of dimethoxyethane as the solvent in the first stage of the Julia olefination³⁸¹ in combination with SmI₂ (see Refs 141 and 142) made it possible to

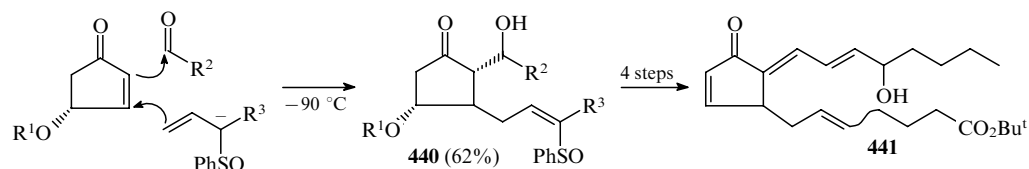
construct trisubstituted C=C bonds, which previously failed, for example, in the synthesis of macrolides of the avermectin–melbemycin series.^{136, 139}

One would expect that considerable study will be given to the enhancement of the stereoselectivity of catalytic Diels–Alder reactions, particularly, involving nonracemic sulfinyl dienes and dienophiles, to the use of new asymmetric building blocks, for example, chiral (*ee* 95%–99%) allylic sulfones synthesised recently,³⁸² and to the development of π -allylic alkylation catalysed by transition metals based on the strategy of the transfer of the reaction centre to the remote functional group (for example, in the synthesis of tetracyclic (–)-dendrobine)³⁸³ with the participation of sulfinyl-containing nucleophiles.

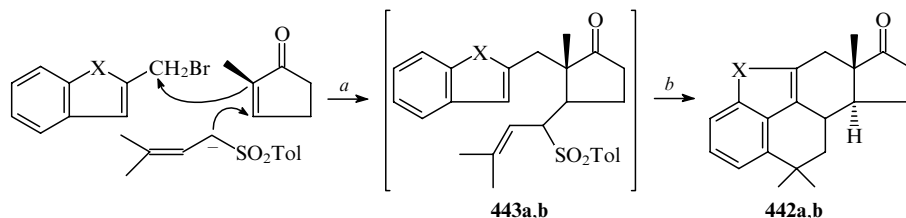
Convergent syntheses (Fuchs²³ took an active part in popularisation of this method) have found a rather wide application in the reactions considered in this review. More modern methodologies, which allow one to perform one-pot syntheses of complex compounds, are not used so often. These procedures are said to be consecutive or tandem processes,^{384–386} cascade reactions,³⁸⁷ processes with the use of counterattacking reagents³⁸⁸ or poly-component condensations.³⁸⁹ The examples of multicomponent reactions considered below demonstrate that this approach to the synthesis of natural compounds is fruitful.

Thus three-component cyclisation of an allylsulfinyl anion with a substituted cyclopentenone and an aldehyde afforded compound **440**. Modification of the latter made it possible to synthesise the prostaglandin derivative **441**.³⁹⁰ Epithio- and epoxyestratetraenones **442a,b**³⁹¹ were synthesised by three-component cyclisation involving the allylsulfonyl anion, which made it possible to construct the steroid skeleton with a high stereoselectivity without isolation of the intermediates **443a,b**. The synthesis of the alkaloids apoyohimbines **444a,b**³⁹² was based on the cascade process involving the Pictet–Spengler reaction of substituted tryptamines with a sulfolene-containing aldehyde, elimination of SO₂ from the intermediates **445a,b** and the intramolecular Diels–Alder reaction. This allows one to perform one-steps introduction of the methoxycarbonyl group at C(22) yielding a pentacyclic reaction product with the stereochemistry of the natural compound (Scheme 15).

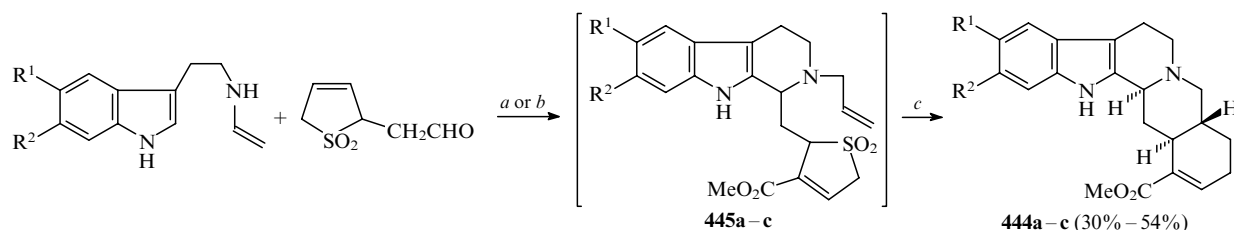
Scheme 15



R¹ = SiMe₂Bu^t, R² = CH=CHCH(OR¹)(CH₂)₃Me; R³ = (CH₂)₃CO₂Bu^t.



X = S (**a**, 92%), O (**b**, 87%); (a) DMF, –78 °C; (b) AlCl₃, 0 °C, 10 min.



R¹ = R² = H (**a**); R¹ = OMe, R² = H (**b**); R¹ = R² = OMe (**c**); (a) AcOH, 20 °C, R¹ = H, OMe; R² = OMe; (b) R¹ = R² = H, CF₃CO₂H, 20 °C; (c) PhMe, Δ , 18 h.

The area of these investigations would be expected to expand in the near future.

When this review had been prepared for publication, the results of new studies devoted to the applications of sulfoxides and sulfones to the synthesis of natural compounds appeared. The most interesting of them are briefly considered below.

Conventional alkylation–desulfonylation of α -sulfonyl carbanions^{393–397} (including those prepared from oxiranes³⁹⁸) along with an interesting version of reductive alkylation of 1,1-di(sulfone) with lithium naphthalenide, allyl bromide or sodium amalgam³⁹⁹ were used for the construction of C–C bonds. Endocyclic C=C bonds were formed by pyrolysis of oxo sulfoxides.^{400, 401} In addition to the coupling of fragments through the (E)-C=C bonds using the classical olefination according to M Julia in the construction of natural molecules,^{402–404} the increasing popularity has acquired a modification of this procedure developed by S Julia⁴⁰⁵ using model compounds (see Refs 406–417 and references cited therein). The procedure elaborated by S Julia involves the reactions of aldehydes with anions generated from 2-benzothiazolyl sulfones whose participation makes it possible to perform olefination as a one-pot process. Double bonds between the pyrrole rings in natural compounds are formed by successive treatment of a mixture of a sulfone and an aldehyde with DBU and $\text{P}(\text{Bu})_3$.⁴⁰⁸ The reactions of α -sulfonyl anions^{409, 410} or anions of chiral sulfoxides⁴¹¹ with carbonyl compounds were used for binding fragments through the CH_2CO or $\text{CH}_2\text{CH}(\text{OH})$ groups. Unsaturated sulfones were involved in cyclisation of acyclic γ -hydroxyvinyl sulfones,^{412–414} metallation of vinyl sulfones at the C=C bond followed by the introduction of a substituent^{415, 416} and [4 + 2] cycloaddition of ethynyl sulfones to *N*-Boc-pyrrole.^{417, 418} Free-radical $\text{Ni}(\text{acac})_2$ -catalysed arylation of optically active sulfoxide with Ph_3ZnMgCl was also reported.⁴¹⁹ The one-pot diastereoselective synthesis of a complex polycyclic compound by cascade cyclisation involving sulfones or sulfoxides under conditions of radical catalysis was described.⁴²⁰

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^b — *Chem. Pharm. J. (Engl. Transl.)*

^c — *Russ. Chem. Bull. (Engl. Transl.)*

^d — *Russ. J. Org. Chem. (Engl. Transl.)*

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‘Living’-chain radical polymerisation

G V Korolev, A P Marchenko

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Abstract. The review is devoted to various types of compounds used as agents for ‘living’ radical polymerisation, such as alkoxyamines formed upon addition of the chain carrier radicals, $R^{\bullet}$, to stable nitroxyl radicals, as well as products of the addition of the radicals to transition metal complexes with different ligands, *etc.* In all cases, the mechanism of the action of these agents consists in their reversible dissociation $A \rightleftharpoons R^{\bullet} + X^{\bullet}$, where $X^{\bullet}$ is a stable free radical or a metal-containing complex which can accept radicals $R^{\bullet}$ ($R^{\bullet} + X^{\bullet} \rightarrow A$) and thus compete with the quadratic chain termination. Particular attention is paid to the studies which allowed a quantitative formulation of the mechanism of ‘living’ radical polymerisation in the form of a mathematical model suitable for predicting both the parameters of the polymerisation and the properties of the resulting polymer (molecular mass and polydispersity). The bibliography includes 359 references.

I. Introduction

‘Living’ radical polymerisation, or, more precisely, ‘living’-chain radical polymerisation is a new line of investigation in the area of radical polymerisation, known from the early 1990s. The origination and development of this area of scientific exploration has become possible owing to the discovery in the last two decades of a new elementary act of polymerisation processes involving the chain carrier radicals $R^{\bullet}$, namely, the reversible addition of $R^{\bullet}$ to several metal complexes or to stable free radicals (in particular, to nitroxyl radicals).

Numerous studies on ‘living’ radical chains (LRC) reported over the last three years (100 articles and more *per annum*) confirm that this new field is of great scientific and technological importance and appears to have considerable promise. Most prominent in this research area are Matyjaszewski’s group in the USA and Fukuda’s group in Japan. In these research groups, studies on

LRC are carried out by polymer chemists in co-operation with mathematicians and physicists, which indicates the high level of scientific co-ordination and financial backing.

This review is concerned with systematisation and critical review of a great body of data on LRC accumulated to date. The authors of the review have worked in the area of LRC since its inception. They appeared to be among the pioneers of the elementary processes which provide the basis for ‘living’-chain radical polymerisation.

II. ‘Living’-chain anionic polymerisation

The concept of a ‘living’ polymer chain or simply a ‘living’ chain (LC) appeared in studies of anionic polymerisation and goes back to Szwarc.¹ He recognised that if a growing polymer anion (a chain carrier, R_A) cannot be quadratically terminated ($R_A + R_A \rightarrow$ ‘dead’ polymer), then, in the absence of reactive impurities (X) capable of breaking the polymer chain following a linear mechanism ($R_A + X \rightarrow$ ‘dead’ polymer), anionic polymerisation proceeds without chain breaking, as a ‘living’ process. In this case, the lifetime (τ) of growing polymer chains exceeds the time necessary for complete conversion (t). In other words, the polymer anions R_A remain ‘living’ not only during the polymerisation, but also following completion of the process, *i.e.*, after complete consumption of the initial monomer. ‘Livingness’ of polymer chains is confirmed by the fact that the polymerisation process restarts upon addition of a fresh portion of the same monomer or any other monomer which can undergo anionic polymerisation at the same centres R_A .

A conventional anionic polymerisation proceeds in such a way that the initiation of R_A is a relatively fast reaction which takes a time interval τ_i much shorter than the time necessary for complete conversion (t). The condition $\tau_i \ll t$ implies that the initiation of all chains occurs nearly simultaneously and that they grow synchronously throughout the polymerisation, so that the number-average molecular mass (M_n) of the resulting polymer is proportional to time. The molecular mass distribution of the polymer chains narrows monotonically as M_n increases and reaches very low values (the polydispersity index, M_w/M_n , approaches a value of 1.0) already at not too high M_n values (several tens of monomer units). This remarkable property is inherent in the ‘living’ chains only ($\tau > t$ and $\tau_i \ll t$). In the case $\tau \ll t$ (short-lived chains), which corresponds to radical polymerisation, the lowest polydispersity of the polymer is either 1.5 or

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2.0 depending on the type of chain termination reaction (disproportionation or recombination).

The use of these valuable properties of the products of 'living' polymerisation has led to design of a novel class of polymeric materials, *viz.*, block copolymers of the $A_nB_mA_n$ type, where A is a polystyrene block, B is a polyisoprene or polybutadiene block, and m and n are the numbers of monomer units in the blocks. At particular m and n values and at the temperatures which are above the glass transition temperature of the elastic block B, but below the glass transition temperature of the block A, these types of copolymers behave as vulcanised rubbers possessing very good physicochemical properties. This is due to a specific structure of the block copolymers, *viz.*, the presence of glassy domains comprising several blocks A arranged regularly in a continuous elastic B-block matrix. The domains playing the role of cross-link points of the polymer network are essentially the same size, which is provided by very low polydispersity of the blocks A. The sizes and regular spatial arrangements of the blocks, which govern the physicochemical properties of the material, depend on n and the m/n ratio. At temperatures above the glass transition temperature of the block A, the copolymer behaves as a nonvulcanised rubber. Depending on temperature, these polymers possess the properties of vulcanisate or devulcanisate. They have played an outstanding role both in the polymer technology and in ecology since in this case the recovery of wastes and exhausted products has become much easier.

At the same time, 'living' anionic polymerisation requires an extremely labour-consuming procedure for the removal of impurities X from an initial reaction system to prevent chain breaking. Additionally, the number of pairs of the monomers of the types A and B is rather limited. Thus, the idea of performing a 'living'-chain radical polymerisation appeared to be quite attractive.

III. 'Living'-chain radical polymerisation

The fundamental distinction between 'living'-chain radical and 'living'-chain ionic polymerisation is that quadratic chain termination is of great importance in the former case and plays a negligible role in the latter. In other words, 'living'-chain radical polymerisation includes deactivation of growing active centres by termination between them ($R + R \rightarrow$ 'dead' polymer).[†] Thus, implementation of 'living'-chain polymerisation requires basically different approaches, since in this case it is the main participant of the polymerisation process rather than a removable (*e.g.*, by purification) impurity that plays the role of chain terminator, which results in a situation where $\tau \ll t$. Therefore, meeting the main condition for 'living' radical polymerisation, $\tau > t$, requires the development of a procedure for extending the lifetime of active centres (chain carriers) R. This also requires the retention of their high reactivities towards the monomer molecules (M) in order to provide the possibility for the polymer chain to grow following the ' $R + M \rightarrow$ chain' mechanism. This means that radicals R should be deactivated in order to preclude quadratic chain termination and, at the same time, should retain their activities in order to provide the polymer chain propagation ($R + M$). At first glance, this problem seems to be intractable.

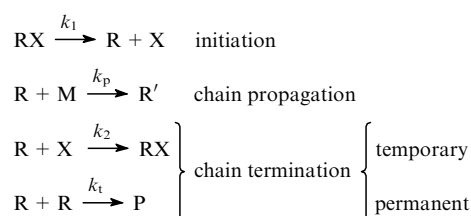
The main advantage of 'living'-chain polymerisation consists in the possibility of obtaining a desired product with narrow polydispersity. At the same time, the second condition necessary for exploitation of this advantage, $\tau_i \ll t$, is also not met in the case of radical polymerisation. Here, initiation of new chains occurs throughout the polymerisation process rather than during a short initial period τ_i , thus disturbing the simultaneous chain propagation and unavoidably increasing the polydispersity of the resulting polymer even in those cases where the lifetime of radical R can be extended to time intervals $\tau > t$.

Eventually, 'living'-chain radical polymerisation seems to have no chance of success. However, a new elementary act of

radical polymerisation has been discovered, namely, temporary entrapment of the chain carrier radical R by an acceptor A ($R + A \rightleftharpoons RA$) followed by release of R (the so-called reversible inhibition). This made it possible to solve both problems, *i.e.*, to extend the time interval τ ($\tau > t$) and to achieve simultaneous propagation of all chains, thus meeting the condition $\tau_i \ll t$. Later, yet another solution to the problem was found, consisting of carrying out the reactions $R^1 + A \rightarrow R^1A$ and $R^1A + R^2 \rightarrow R^2A + R^1$, where R^1 and R^2 are the growing polymer chains of the same nature but different lengths, and/or the growing chains of different nature. Mention may be made that these two solutions differ only in the type of regeneration of the entrapped (accepted) chain carrier radicals. In the former case, the RA adduct dissociates into the initial components, whereas in the latter case the entrapped chain carrier radical R^1 is released from the R^1A adduct following the radical substitution reaction $R^1A + R^2 \rightarrow R^2A + R^1$.

Among the substances suggested for the use as acceptors A are stable free radicals R_s (nitroxyl radicals, triphenylmethyl, *etc.*) and metal complexes (porphyrin, phthalocyanine and cobaloxime cobalt complexes, copper and iron complexes with halide and organic ligands, *etc.*). Active chain carrier radicals R react with stable radicals R_s to give adducts in which the $R-R_s$ covalent bond is relatively weak and thus can dissociate at 373–423 K. For instance, if R is a growing polystyrene chain and R_s is a stable nitroxyl radical, the bond strength in the $R-R_s$ adduct is estimated at $E = 125.4 \text{ kJ mol}^{-1}$, which provides a rather high rate constant for bond dissociation, $k_1 = 10^{-4} - 10^{-5} \text{ s}^{-1}$, already at 373 K.

First, let us consider the above-mentioned elementary reactions as applied to the problem of 'living' chains taking the $R + A \rightleftharpoons RA$ reaction as an example. Let us denote the rate constants for dissociation and reverse recombination as k_1 and k_2 , respectively, the acceptor A as X (in order to specify it as a stable free radical) and the adduct as RX. If RX is used instead of conventional initiators (peroxides, azodinitriles, *etc.*) of radical polymerisation, the mechanism of the process can be described by the following scheme:



Scheme 1

At particular values of rate constants k_1 , k_2 , k_p and k_t , this four-stage mechanism provides a negligible contribution of chain termination reactions. Provided that $k_1[R] \ll k_2[X]$, the prevailing chain 'termination' by the $R + X$ reaction simply makes the chain temporarily inactive (a 'dormant' chain, RX) until the next dissociation act of RX. In such a manner the condition $\tau > t$ is met. In the final stage of polymerisation (after complete consumption of the initial monomer), almost all chains, except for a small fraction of 'dead' (quadratically terminated) chains that form a conventional random (statistical) polymer P, appear to be 'dormant' in the form of RX. Obviously, the addition of a fresh portion of the initial or another monomer (if a block copolymer is synthesised) will re-activate the chain carriers R, which means that the situation will be quite adequate to a 'living' polymerisation.

To meet the second essential condition, *viz.*, simultaneous chain initiation ($\tau_i \ll t$), it is sufficient that the half-life of the adduct RX, equal to $0.69/k_1$, be much (10 to 100 times) shorter than the time necessary for complete conversion, t . Provided that $0.69/k_1 \ll t$, each growing chain manages to be both in active and 'dormant' state tens or hundreds times. This synchronising mechanism of chain propagation provides a very low polydispersity of the polymer. It should be noted that corresponding fitting procedure for numerical values of rate constants uses the k_1 and k_p

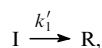
[†] Hereafter, in some instances the radical sign will be omitted for simplicity.

constants as well as the temperature (taking into account the temperature dependence of k_1 and k_p) as independent variables.[‡]

Thus, the use of acceptors X that temporarily entrap the chain carrier radical R and then release the initial species X and R makes it possible to solve the problem of implementation of a 'living'-chain radical polymerisation. Unlike anionic polymerisation in which the chain carrier cannot undergo quadratic chain termination at all, it is appropriate to call the process discussed above a pseudo-'living' polymerisation (and, correspondingly, to consider pseudo-'living' chains), since the radical chains propagate only in the form of active chain carriers R following their 'recovery' from the 'dormant' state and thus can undergo quadratic termination.

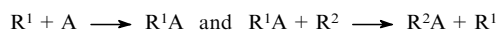
It should be noted that the four-stage process discussed above is a non-steady-state process. Therefore, correct quantitative estimates of the parameters of the process can be obtained only after solving corresponding systems of differential equations rather than algebraic equations, as is the case of a steady-state process.

Finally, mention may be made that a 'living'-chain radical polymerisation process following this mechanism is stable towards such disturbing factors as additional initiation



where I is an initiator supplied from an external source or the monomer itself (self-initiation involving the monomer molecules occurs, *e.g.*, in the styrene polymerisation at temperatures above 373 K). Provided that the $k'_1[I]$ value is at least 5 to 10 times smaller than the $k_1[RX]$ value, this disturbing factor can be ignored. This condition can be met, as will be shown in the next Sections of the review dedicated to consideration of particular experimental data.

The other type of 'living'-chain polymerisation using the following elementary stages,



differs from that discussed above (using the $R + A \rightleftharpoons RA$ reaction) only in that it requires the use of an initiator I (or the process should be performed under conditions of spontaneous initiation involving the monomer), since the R^1A adduct does not initiate polymerisation.[§]

IV. The progress in investigations on 'living'-chain polymerisation

The progress in studies on 'living'-chain radical polymerisation can be divided into three stages.

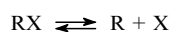
1. The discovery of temporary entrapment of chain carrier radicals R by compound A with the formation of labile adducts $R-A$ from which R can be released by dissociation (or following a radical substitution reaction, as was shown later). This phenomenon was called reversible inhibition.

2. The use of reversible inhibition for designing a 'living'-chain radical polymerisation process (theoretical analysis, experimental studies).

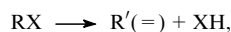
3. Implementation of 'living' chain radical polymerisation following a procedure which includes an exhaustive system of proofs of successful polymerisation (registration of changes in the average molecular mass, molecular mass distribution and other characteristics during monomer conversion).

It is hard to mention a pioneering work for stages 1 and 2. More correct is to consider a number of pioneering studies carried out independently by investigators from different research groups.

However, the third stage undoubtedly began with a pioneering study carried out by investigators from Canada.² Taking the radical polymerisation of styrene in the presence of a stable iminoxyl radical (X) as an example, they were the first to show that the chain carrier (the growing polystyrene chain) R is alternately present in the reaction system in the deactivated (in the form of adduct RX) and active (in the form of free radicals $R + X$) states. This was proved by corresponding kinetic studies and by measurements of molecular mass distribution and average molecular mass of the resulting polymer during the conversion. Unlike unsuccessful attempts of their predecessors, the success of investigators from this research group is due to an extremely fortunate (chance or predicted?) choice of styrene as the monomer, since the presence of a phenyl substituent in the α -position with respect to the $R-X$ bond, which undergoes dissociation, makes this bond more labile, which allows its dissociation at a sufficiently high rate at temperatures below 423 K. This fact appeared to be essential since at $T > 423$ K the contribution of hydride transfer accompanying the dissociation increases and the dissociation mechanism changes from reversible



to irreversible



where $R' (=)$ denotes the 'dead' (terminated by intramolecular disproportionation) polystyrene chain with the end group containing a double bond and XH is the corresponding hydroxylamine.

This pioneering work² initiated the appearance of numerous publications and their number seems to have no limit as yet. At the same time, it should be remembered that the communication cited was preceded by a number of experimental and theoretical studies carried out at the first two stages. A scheme of the development of investigations in the area of 'living' polymerisation is presented below (Scheme 2).

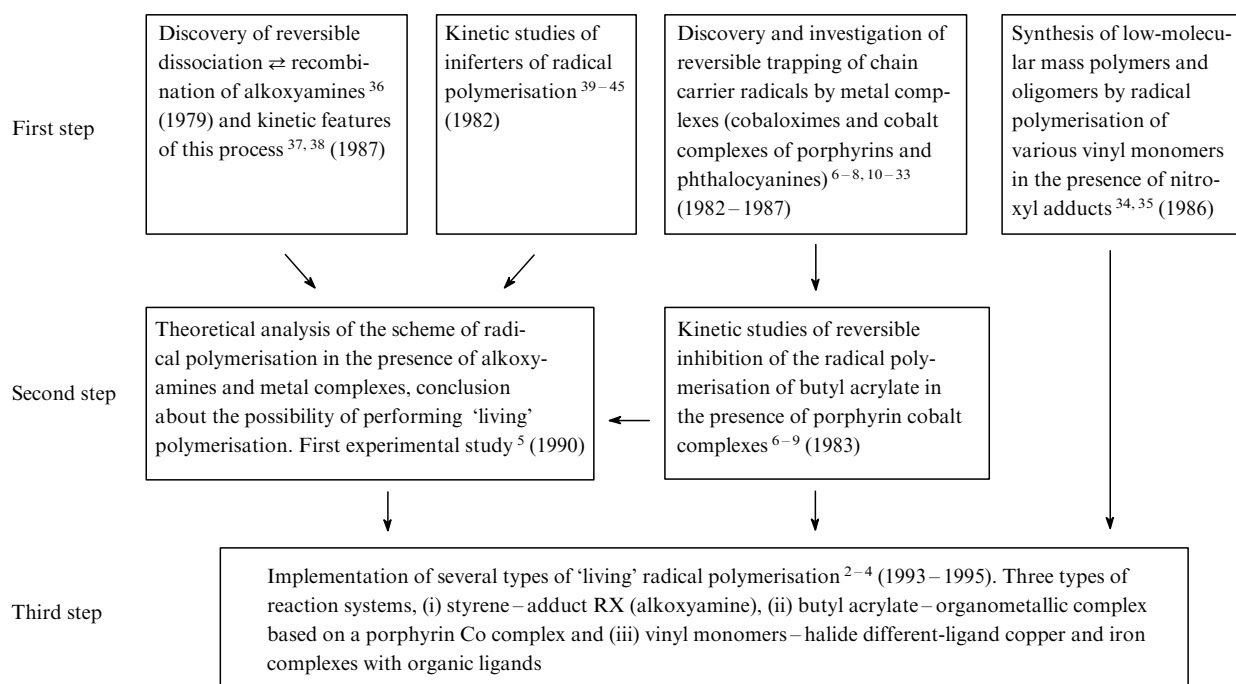
This scheme of pioneering studies may seem to be too cumbersome and overburden with details; however, it reflects the state-of-the-art in this area. First, at first glance different-type and non-related phenomena have been observed in studies of compounds of different chemical nature, such as alkoxyamines, macrocyclic cobalt compounds (later, copper and iron complexes), dithiocarbamates, *etc.* These studies were carried out concurrently and independently. Then, it was appreciated that, despite different chemical nature of compounds studied, all of them obey identical kinetic regularities as regards their ability to entrap temporarily (reversibly) active free radicals (including growing polymer chains) and release them after certain time intervals. Simultaneously, the investigators perceived the possibility of using this type of acceptors ('trappers') as agents for 'living' radical polymerisation. (This was best shown by Smirnov.⁵) Then, several types of 'living'-chain polymerisations were reported (each of these studies formed the basis for an independent investigation line). Further development of these investigation lines is based on these initial pioneering works.

In conclusion, it should be noted that we cannot say unambiguously who was the pioneer of 'living'-chain anionic polymerisation. Undoubtedly, Szwarc^{1,46,47} has not only systematised and thoroughly analysed the key phenomena related to 'living' carbanions, thus having created a well-founded scientific discipline, but was also the first who discovered many of these phenomena. Nevertheless, his studies were preceded by investigations of other researchers. As early as 1936, Abkin and Medvedev⁴⁸ developed an original procedure for the determination of the lifetime (τ) of growing carbanion polymer chains and found that for anionic polymerisation of butadiene catalysed by sodium metal the τ value is so long that it exceeds the time necessary for complete conversion of the monomer. In other words, they discovered a 'living' chain carrier carbanion and established that the polymerisation proceeded without chain breaking (in a 'living' manner). However,

[‡] The rate constants k_2 and k_t depend only slightly on both the nature of the reagents (R and X) and the temperature (their numerical values lie within the limits $10^7 \leq k_2 \leq 10^8$, $10^7 \leq k_t \leq 3 \times 10^7$ litre mol⁻¹ s⁻¹).

[§] The only exception are metal halide-alkyl halide systems in which free radicals can be generated (see Section VI).

Scheme 2



this study received little attention and in 1956 Szwarc *et al.*^{46,47} re-discovered 'living' polymerisation of vinyl monomers as though it were a new phenomenon.

V. Alkoxyamines as agents for 'living'-chain radical polymerisation

1. A brief history of investigations

As long ago as the 1970s, it was found^{36,37} that entrapment of active free (*e.g.*, polymethacrylate) radicals *R* by stable free (*e.g.*, iminoxyl) radicals *X* at moderate temperatures (below 323 K) results in the formation of stable adducts *RX* (alkoxyamines) which can release the initial radicals *X* and *R* upon raising the temperature to 373–423 K. More recently, this property of the adducts *RX* was used to perform one of the first 'living' radical polymerisations.⁵ Other stable (*e.g.*, phenylmethyl) radicals were also tried as *X*;^{49,50} however, these attempts failed. In majority of studies, nitroxyl radicals were used, which react with hydrocarbon chain carrier radicals to give the corresponding alkoxyamines.

First of all, mention should be made of the pioneering works^{5,37,38} (see Scheme 2), as well as of the studies in which alkoxyamines were used as initiators.^{34,51–55} It is these studies that best showed the salient features of 'living'-chain polymerisation, namely, a reduction of polydispersity and an increase in molecular mass during monomer conversion and the correspondence between the number of growing polymer chains (*n_c*) and that of alkoxyamine molecules introduced into the system (*n_a*). This correspondence means that at any degree of conversion (*Γ*), the following relationship is valid

$$\Gamma[M]_0 \frac{M_M}{M_n} = n_c = n_a,$$

where $[M]_0$ is the concentration of A monomer in the initial system, M_M is the molecular mass of the monomer and M_n is the number-average molecular mass of the polymer at a given degree of conversion.

These publications^{34,51–54} were followed by a number of studies^{2,56–61} in which alkoxyamines were synthesised *in situ* from nitroxyl radicals introduced into the polymerisation system and radical initiators (peroxides, azodinitriles). The initiators were chosen so that their half-lives would be a factor of several tens or even several hundreds shorter than the time necessary for

complete conversion. Polymerisation of monomers in the presence of nitroxides (without added initiators) also belongs to processes in which alkoxyamines are synthesised *in situ*. The reaction is self-initiated by the monomer, as is the case of autopolymerisation of styrene.^{61–65}

Studies dealing with the development of procedures for modification of alkoxyamines by catalytic amounts of strong organic acids or other compounds aimed at improving their efficiency occupy a special place.^{61,66–68} However, such a modification has little effect and its mechanism is still to be clarified.

The most serious drawback of alkoxyamines as agents for 'living' polymerisation is that they are effective only in the polymerisation of styrene and its derivatives.^{69–72} For other monomers, alkoxyamines appear to be rather ineffective. They find a limited application to homopolymerisation of polar monomers (acrylates, methacrylates)^{61,73–78} and their copolymerisation with some other monomers.^{79–83} The most plausible reason for reduction of the efficiency of alkoxyamines in the polymerisation of polar monomers is that the C–ON bond in their molecules is too strong. The temperature necessary for dissociation of this bond at sufficient rate is too high, so that irreversible intramolecular disproportionation occurs instead of reversible dissociation into the initial radicals *R* and *X*. This irreversible reaction results in the formation of inert products, *viz.*, a hydroxylamine and an unsaturated compound *R*(=) with the terminal double bond. In styrene and its derivatives, as well as in the copolymers of styrene with polar monomers, the C–ON bond is weakened because of the effect of phenyl substituent.^{84,85} In the copolymerisation of styrene with polar monomers, the weakening effect of the styrene unit is achieved through the polar monomer unit⁸⁵ (the effect of the penultimate unit).

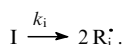
2. Synthesis of alkoxyamines

Several methods for the synthesis of adducts R_iM_nX , where R_i is the initiator radical (*e.g.*, $\text{Ph}-\text{CO}-\text{O}^\bullet$ formed upon decomposition of dibenzoyl peroxide, or BPO), *M* is the monomer (*e.g.*, styrene) and *X* is the nitroxyl radical (*e.g.*, 2,2,6,6-tetramethyl-1-piperidinyloxy, or TEMPO) have been reported.^{34,51–55} Depending on the composition, *i.e.*, the $[R_i]:[X]:[M]$ ratio in the reaction mixture, adducts with different content of *M* (from *n* = 1 to *n* ≈ 10) can be obtained. Obviously, these methods are effective only under the reported reaction conditions.^{34,51–55} Later, the

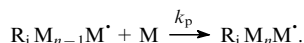
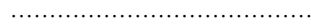
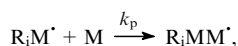
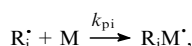
possibility of designing the syntheses of any adducts of the R_iM_nX type has been demonstrated.⁸⁶ A mathematical method was developed for calculation in the steady-state approximation of the yields of the adducts synthesised in the polymerisation processes described by the simplified Scheme 3 which includes the initiation, chain propagation and chain termination stages. This scheme assumes that only a linear chain termination occurs in the system (quadratic chain termination can be ignored because of a very high concentration of an agent X responsible for the linear chain termination).

Scheme 3

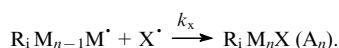
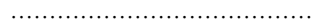
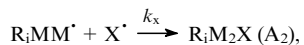
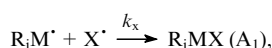
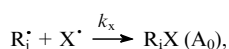
Initiation (zeroth stage)



Chain propagation (first stage)



Chain termination (second stage)



Here I is the initiator; X^* is the stable free radical; M is the monomer; R_i^* , R_iM^* , ..., $R_iM_{n-1}M^*$ are active free radicals and A_n are products of the corresponding reactions.

Analysis of Scheme 3 makes it possible to derive the following expressions for instantaneous rates of formation of any adduct, from A_0 to A_n , during the synthesis.

$$\frac{d[A_0]}{dt} = k_x[X][R_i] = \frac{W_i k_x [X]}{k_{pi}[M] + k_x[X]} = W_i \frac{1}{k_{pi}[M]/k_x[X] + 1}, \quad (1)$$

$$\begin{aligned} \frac{d[A_1]}{dt} &= k_x[X][R^1] = \frac{W_i k_x [X] k_{pi} [M]}{(k_{pi}[M] + k_x[X])(k_p[M] + k_x[X])} = \\ &= \frac{d[A_0]}{dt} \frac{1}{k_p/k_{pi} + k_x[X]/k_{pi}[M]}, \end{aligned} \quad (2)$$

$$\begin{aligned} \frac{d[A_2]}{dt} &= k_x[X][R^2] = \frac{W_i k_x [X] k_{pi} [M] k_p [M]}{(k_{pi}[M] + k_x[X])(k_p[M] + k_x[X])^2} = \\ &= \frac{d[A_1]}{dt} \frac{1}{k_x[X]/k_p[M] + 1}, \end{aligned} \quad (3)$$



$$\begin{aligned} \frac{d[A_n]}{dt} &= k_x[X][R^n] = \frac{W_i k_x [X] k_{pi} [M] (k_p [M])^{n-1}}{(k_{pi}[M] + k_x[X])(k_p[M] + k_x[X])^n} = \\ &= \frac{d[A_1]}{dt} \left(\frac{1}{k_x[X]/k_p[M] + 1} \right)^{n-1}, \end{aligned} \quad (4)$$

where W_i is the rate of initiation and $R^1 = R_iM$, $R^2 = R_iM_2$, ..., $R^n = R_iM_n$.

For any stage of the synthesis, the yield (Y) of each adduct A_n at instant t is calculated by the formula

$$Y = \int_0^t \frac{d[A_n]}{dt} dt, \quad (5)$$

where the form of the function describing the dependence of $d[A_n]/dt$ on t is given by formulae (1)–(4) which take into account the dependences of the concentrations of all reagents on time.

The dependence of $[I]$ on t is described by the familiar integral of the rate of a unimolecular reaction

$$[I]_t = [I]_0 \exp(-k_i t), \quad (6)$$

while the dependence of $[X]$ on t is given by the equation

$$[X]_t = [X]_0 - 2f([I]_0 - [I]_t) = [X]_0 - 2f[I]_0[1 - \exp(-k_i t)], \quad (7)$$

where f is the fraction of free radicals that did not undergo intracage recombination (this quantity is also called the efficiency of initiation, $f \approx 0.5$). From Eqn (7) it follows that the concentration of stable radical X at instant t is equal to the difference between the initial concentration of this radical, $[X]_0$, and the concentration of free radicals generated by the time t as a result of the decomposition of the initiator I.

If the synthesis is carried out under standard conditions (the monomer is taken in a large excess, $[M]_0 \gg [I]_0 \approx [X]_0$), the concentration $[M]$ is constant at any instant. If the synthesis is performed either under specific conditions (without a large excess of M) or in such a way that the adducts R_iM_nX with large n values are obtained, the form of the function $[M]_t$ is determined by the integral of the stationary rate $d[M]/dt$. For long chains ($n > 10$), the following approximation is valid

$$-\frac{d[M]}{dt} \approx \frac{k_p[M]}{k_x[X]} W_i, \quad (8)$$

whence, taking into account expressions (6) and (7), it follows that

$$[M] = [M]_0 \exp\left(-\frac{k_p k_i}{k_x} \psi\right), \quad (9)$$

where

$$\psi = \int_0^t \frac{[I]_t}{[X]_t} dt = \int_0^t \frac{[I]_0 \exp(-k_i t)}{[X]_0 - 2f[I]_0[1 - \exp(-k_i t)]} dt. \quad (10)$$

This calculation procedure makes it possible to predict the results of synthesis and to choose optimum conditions, since the values of all constants (k_i , k_{pi} , k_p and k_x) appearing in Eqns (1)–(10) can be rather accurately estimated from the reported data (see, e.g., Ref. 87). The results of calculations for the styrene–TEMPO–BPO system, obtained for three temperatures, are listed in Table 1.

The reliability of the calculations has been confirmed experimentally. Both the type of the main adduct ($A_1 = R_iMX$) and its content ($[A_1]/100 \sum_n [A_n] > 90\%$) in the overall product $\sum_n A_n$

nearly coincide with the corresponding calculated data. As can be seen from Table 1, the target product A_1 is the main product in the temperature range 348–368 K.

According to calculations, non-peroxide compounds (e.g., azonitriles) are unsuitable for use as initiators since only peroxide radicals R_i with the free valence at the oxygen atom ensure a rather high value of the k_{pi}/k_p ratio (several orders of magnitude). If the values of k_{pi} and k_p are comparable, the adduct R_iX ($n = 0$) is formed as the main product instead of the target R_iM_nX adduct. However, R_iX cannot be used as the agent for ‘living’ polymerisation because its C–ON bond energy is too high.

The results of calculations for the styrene–TEMPO–dicyclohexyl peroxydicarbonate (DCPDC) system⁸⁶ (Table 2) imply that the main adduct is

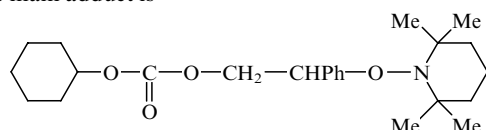


Table 1. Results of calculations of the yields of the adducts R_iM_nX in the course of 'living' polymerisation of styrene (M) in the presence of stable free radicals X (TEMPO) and initiator (BPO).

T/K	$10^5 k_i$ / s^{-1}	k_p (see ^a)	$10^{-7} k_x$ (see ^a)	$10^{-5} k_{pi}$ (see ^a)	Yields of adducts $A_0 \times 10^6$, $A_1 \times 10^4$, and $A_2 \times 10^5$ (mol litre ⁻¹) after every hour from the beginning of the process					
					1	2	3	4	5	6
348	2.6	262	1.8	10.2	3.5, 3.8, 1.0	6.2, 6.9, 2.0	8.3, 9.5, 2.8	9.9, 11.6, 3.5	11.2, 13.4, 4.2	12.2, 15.0, 4.7
358	8.3	352	2.1	12.5	5.2, 5.7, 1.8	8.6, 9.9, 3.3	10.8, 13.1, 4.5	12.4, 15.4, 5.4	13.5, 17.1, 6.0	14.3, 18.4, 6.8
368	25.2	464	2.6	15.2	10.8, 13.1, 4.9	14.1, 18.3, 7.4	15.3, 20.4, 8.5	15.8, 21.3, 9.0	16.0, 21.7, 9.3	16.1, 21.8, 9.4

Note. Initial concentrations: $[TEMPO] = 4.8 \times 10^{-3}$ mol litre⁻¹, $[BPO] = 2.3 \times 10^{-3}$ mol litre⁻¹. ^a Dimensionality is litre mol⁻¹ s⁻¹.

Table 2. Results of calculations of the yields of adducts in the course of 'living' polymerisation of styrene using DCPDC as the initiator.

T/K	$10^5 k_i$ / s^{-1}	k_p (see ^a)	$10^{-7} k_x$ (see ^a)	$10^{-5} k_{pi}$ (see ^a)	Yields of adducts $A_0 \times 10^6$, $A_1 \times 10^4$, and $A_2 \times 10^5$ (mol litre ⁻¹) after every hour from the beginning of the process					
					1	2	3	4	5	6
323	3.0	117	1.0	5.8	4.0, 4.3, 0.9	6.9, 7.8, 1.8	9.1, 10.6, 2.5	10.8, 12.9, 3.1	12.0, 14.7, 3.7	13.0, 16.2, 4.1
333	12.0	164	1.3	7.3	10.8, 12.8, 3.5	14.3, 18.2, 5.3	15.6, 20.5, 6.2	16.1, 21.5, 6.6	16.3, 21.9, 6.8	16.4, 22.1, 6.9
343	44.5	226	1.6	9.1	16.0, 21.2, 7.1	16.4, 22.0, 7.5	16.5, 22.1, 7.6	16.5, 22.1, 7.6	16.5, 22.1, 7.6	16.5, 22.1, 7.6

Note. Initial concentrations: $[TEMPO] = 4.8 \times 10^{-3}$ mol litre⁻¹, $[BPO] = 2.3 \times 10^{-3}$ mol litre⁻¹. ^a Dimensionality is litre mol⁻¹ s⁻¹.

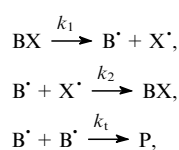
Dicyclohexyl peroxydicarbonate decomposes into radicals much faster than BPO (for DCPDC, the k_i value is 100 times greater than for BPO). This allows implementation of syntheses at lower temperatures, which is an additional 'insurance' against the risk of possible side reactions due to dissociation of R_iM_nX and ignored in Scheme 3.

According to calculations, there is little point in synthesising the adducts with long polystyrene chain ($n \approx 10$) using a one-step process. In this case, a considerable amount of hard-to-remove contaminating adducts of nearly identical compositions can be formed, even if a very carefully 'adjusted' procedure with optimum 'recipe' is employed. Because of this, long-chain adducts R_iM_nX ($n = 10$) should be synthesised using a two-step procedure which includes (i) the synthesis of R_iMX ($n = 1$) and (ii) a controlled 'living' bulk polymerisation of M (in order to extend the M_n block until desired molecular mass value) at a higher temperature at which the rate of reversible dissociation of R_iMX is high enough. In such a manner, it is possible to extend the polymer chains by about 10 units over a period of 3–4 h at 393 K and to obtain the $R_iM_{10}X$ adducts with a polydispersity index of 1.15 and more (GPC data).

It thus follows that currently the synthesis of alkoxyamines is developed to the extent that it can be performed as a kinetically controlled process with accurate prediction of results.

3. Determination of the rate constant of reversible dissociation of alkoxyamines at the C–ON bond

Reversible dissociation of R_iM_nX (BX), which is the 'heart' of the mechanism of 'living'-chain radical polymerisation, is described by Scheme 4.



Scheme 4

where P is the recombination (or disproportionation) product of radicals $\text{B}^\cdot$ and $k_2 \approx k_t \approx 10^7\text{--}10^8$ litre mol⁻¹ s⁻¹.

Since dissociation of BX is a non-steady-state process, running concentrations of all compounds involved in the process can only be found after solving the system of differential equations (11)–(13).

$$\frac{d[\text{B}]}{dt} = k_1[\text{BX}] - k_t[\text{B}]([\text{B}] + [\text{X}]), \quad (11)$$

$$\frac{d[\text{X}]}{dt} = k_1[\text{BX}] - k_t[\text{B}][\text{X}], \quad (12)$$

$$\frac{d[\text{BX}]}{dt} = -k_1[\text{BX}] + k_t[\text{B}][\text{X}], \quad (13)$$

$$[\text{BX}] = [\text{BX}]_0 - [\text{X}], \quad (14)$$

$$[\text{P}] = [\text{X}] - [\text{B}]. \quad (15)$$

The following analytical solutions of the system of equations (11)–(15) were obtained for a time interval $(k_1 k_t [\text{BX}]_0 / 3)^{-1/2} \ll t \ll (k_t [\text{BX}]_0 / 24 k_1^2)$ which covers almost entirely the range of practically significant t values (from fractions of a second to tens of days)⁸⁸:

$$[\text{X}] = [\text{BX}]_0 \left(\frac{3 k_1^2 t}{k_t [\text{BX}]_0} \right)^{1/3}, \quad (16)$$

$$[\text{B}] = [\text{BX}]_0 \left(\frac{k_1}{3 k_t^2 [\text{BX}]_0^2 t} \right)^{1/3}. \quad (17)$$

From Eqn (16) it follows that if the k_t value is estimated to sufficient accuracy, the value of

$$k_1 = \frac{[\text{X}]^{3/2} k_t^{1/2}}{[\text{BX}]_0 (3t)^{1/2}} \quad (18)$$

can be determined in the experiments on the decomposition of BX in inert media from the ESR measurements of the kinetics of accumulation of radicals $\text{X}^\cdot$. The most reliable k_t estimate is $k_t \approx 10^7\text{--}10^8$ litre mol⁻¹ s⁻¹. From Eqn (15) it follows that the data on the kinetics of accumulation of P can be used instead of the corresponding data for $\text{X}^\cdot$ if time t is rather long and $[\text{X}] \gg [\text{B}]$. This can be done if for any reason it is more convenient to perform experimental measurements of [P].

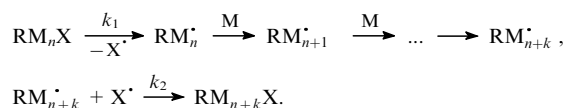
In most cases, ESR measurements of the kinetics of accumulation of radicals $\text{X}^\cdot$ in order to determine the k_1 value are carried out under conditions of reversible decomposition of alkoxyamines.^{85, 89–91}

Recently,⁹² yet another procedure for the measurement of the k_1 values has been developed. It includes measurements of the

consumption of radical $B^{\bullet}$ in the reaction with benzoquinone (BQ), which is a highly efficient acceptor of radicals $B^{\bullet}$, instead of measuring the consumption of $B^{\bullet}$ in the reaction $B^{\bullet} + X^{\bullet}$. Each BQ molecule entraps two radicals $B^{\bullet}$ with the rate constant $k_x \approx 10^5 \text{ litre mol}^{-1} \text{ s}^{-1}$ (for styryl radical at $T = 333\text{--}353 \text{ K}$). If benzoquinone ($\sim 10^{-2} \text{ mol litre}^{-1}$) is introduced into the system, then, according to Scheme 4, the deactivation rate of radicals $B^{\bullet}$ by BQ will be $W_x = k_x[BQ][B] = 10^3[B]$ while the rate of the reverse transformation of $B^{\bullet}$ into BX will be $W_2 = k_2[X][B] = 10^2[B]$ (according to ESR data, $[X] \approx 10^{-6} \text{ mol litre}^{-1}$ at $k_2 \approx 10^8 \text{ litre mol}^{-1} \text{ s}^{-1}$). Thus, the addition of BQ decreases the rate of the reverse reaction in Scheme 4 by at least an order of magnitude, which is tantamount to nearly complete suppression of this reaction.

Under these conditions, the rate of accumulation of $X^{\bullet}$ as obtained from ESR measurements will be virtually equal to the rate of dissociation of BX. This method for the determination of k_1 eliminates difficulties associated with side reactions ignored by Scheme 4, such as, *e.g.*, disproportionation of BX with the formation of XH and a polymer $P(=)$ with a double bond in the end group. The side reactions transform a paramagnetic species $X^{\bullet}$ into an 'ESR stealth', thus disturbing the results of measurements. The new method⁹² is also more advantageous than that reported by Fischer⁸⁸ because the k_1 constant is determined here without using the k_t value, which can only be determined with an accuracy of an order of magnitude. Therefore, the accuracy of the new method is higher by an order of magnitude.

An original method for measurement of the constant k_1 was suggested.⁹³ Here, the k_1 value is determined separately rather than in combination with the k_t value. This is achieved by performing the measurements in the bulk of the monomer. In this case, owing to the reaction with the monomer, the active dissociation product of the initial alkoxyamine (RM_nX), *viz.*, a hydrocarbon radical $RM_n^{\bullet}$, manages to extend its chain by several monomer units before the next act of conversion into alkoxyamine as a result of the reaction with iminoxyl.

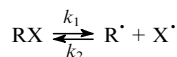


This procedure makes it possible to distinguish between the initial alkoxyamine RM_nX and 'heavy' alkoxyamines $RM_{n+k}X$, $RM_{n+2k}X$, ..., $RM_{n+mk}X$ and allows determination of k_1 from the data on the decrease in the concentration of the initial RM_nX . The reversible character of the dissociation presents no problems to determination of the constant k_1 , since only the first acts of dissociative decomposition of each initial molecule RM_nX are measured experimentally. The next decomposition acts that follow the reversible reduction involve compound $RM_{n+mk}X$ ($m = 1, 2, \dots$) for which no measurements have been performed.

A procedure for separate determination of the concentration of the initial alkoxyamine RM_nX (M is styrene, $n = 1$) in the mixture with 'heavy' alkoxyamines $RM_{n+mk}X$ using gel-permeation chromatography has been developed.⁹³ For $n = 1$, the peak of the initial alkoxyamine on the chromatogram of the mixture can be resolved to an accuracy of 10%–20%, which is correspondingly the accuracy of the determination of k_1 . The k_1 values thus obtained [$k_1 = 2.0 \times 10^{13} \exp(-124200/RT) \text{ s}^{-1}$] should be considered the most reliable. The limitation inherent in this method is due to the fact that it can only be applied to alkoxyamines containing one monomer unit per molecule. For $n > 1$, the resolution of the peak of the initial compound in a mixture of substances containing $n + mk$ monomer units decreases substantially. From this viewpoint, the use of the new method⁹² discussed above (competitive entrapment of active hydrocarbon radicals by benzoquinone) seems to be more convenient for $n > 1$, since it has no limitations as regards the n values for the initial alkoxyamine.

The method for assessing the constant k_1 in combination with k_p and k_t , based on measurement of the k_1k_p/k_t ratio appears to be

the most popular.^{58,89,94–101} This requires plotting the kinetic curve $W_M(t) = -d[M]/dt = k_p[M][R]$ and the curve of accumulation of the iminoxyl radical $[X]_t$. If the equilibrium in a system



is established much faster than any perturbation (*e.g.*, the reaction $R^{\bullet} + R^{\bullet}$) is developed, the function $[X]_t$ can be calculated using the formula $[X]_t = k_1[RX]/k_2[R]$, where the concentrations of RX and $R^{\bullet}$ depend on t . The $[RX]$ value is determined from the relationship $[RX] = [RX]_0 - [X]_t$, where $[RX]_0 \approx 10^{-2} \text{ mol litre}^{-1}$ and $[X]_t \approx 10^{-6}\text{--}10^{-5} \text{ mol litre}^{-1}$. Hence to sufficient accuracy we get $[RX] \approx [RX]_0$.

For a fixed $t = t_f$, the $[R]$ value is determined from the kinetic curve $[R] = W_M(t_f)/k_p[M]$, where $[M]$ is the running concentration at the same instant $t = t_f$. Then, by comparing the $W_M(t)$ and $[X]_t$ curves for the same t we can calculate the ratio

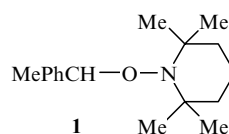
$$\frac{k_1k_p}{k_2} \approx \frac{[X]_t W_M(t)}{[RX]_0[M]}.$$

Reliability of calculations can be checked for independence of the parameter k_1k_p/k_t on the conversion time t . The accuracy of the estimate of the constant k_1 by this method is also obviously dependent on the reliability of the values chosen for k_p and k_t . Usually, the values $k_p = 2 \times 10^3$ (for $T = 393 \text{ K}$)¹⁰² and $k_t = 10^7\text{--}10^8 \text{ litre mol}^{-1} \text{ s}^{-1}$ are used. As a rule, calculations of 'living' polymerisation processes are carried out using the constant k_1 in the form of the ratio $K = k_1/k_2$ (the equilibrium constant), thus it is the equilibrium constant value that is the main goal of quantitative estimates reported in many studies.

Nevertheless, it should be noted that the scatter of k_1 values reported by different authors is extremely wide and, which is most important, the reasons for this phenomenon are unclear. For instance, the rate constant of dissociation of 1-phenyl-1-(2,2,6,6-tetramethylpiperidinyl-1-oxy)ethane (**1**) in deuterated styrene was reported to be $\sim 10^{-3} \text{ s}^{-1}$ at 396 K.¹⁰³ On the other hand, the k_1 value obtained for the dissociation of the same compound at a higher temperature (413 K) was reported¹⁰⁴ to be equal to $\approx 8 \times 10^{-5} \text{ s}^{-1}$ (dissociation in tetrachlorobenzene). Such a wide scatter in the k_1 values can hardly be explained by the solvent effect alone.

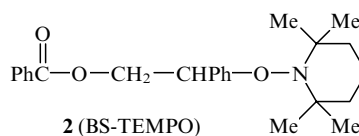
In conclusion, let us dwell on the side reaction of irreversible dissociation of alkoxyamines which occurs at high temperatures (above 408–433 K). Apparently, it is this reaction that makes alkoxyamines with increased (as compared to styrene-containing derivatives) strength of the C–ON bond 'inoperative'.

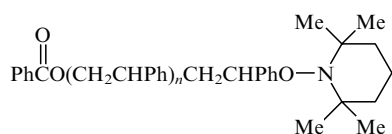
This side reaction was first studied taking a model alkoxyamine **1** as an example.¹⁰⁴



It was concluded that dissociation of this alkoxyamine with the cleavage of the C–ON bond follows two pathways resulting in (i) an active hydrocarbon radical and the TEMPO stable radical and (ii) hydride transfer to give an unsaturated hydrocarbon and hydroxylamine.

The competition between the two types of cleavage of the C–ON bond was studied in detail by high-resolution NMR spectroscopy¹⁰⁵ taking alkoxyamines obtained upon radical decomposition of dibenzoyl peroxide in styrene as examples.





3 (PS-TEMPO with $M_n = 1100$, $M_w/M_n = 1.03$)

Thermal decomposition of alkoxyamines **2** and **3** was performed in perdeuterated toluene in the temperature range 393–433 K. The products obtained during the conversion were analysed by ^1H NMR spectroscopy. This required preliminary assignment of the ^1H NMR spectra of mixtures using the ^1H NMR spectra of model compounds and specially developed auxiliary calibrations. The obtained rate constants (k_{dec}) of irreversible decomposition of alkoxyamines **2** and **3** were $4.7 \times 10^{14} \exp(-157\,000/RT)$ and $5.7 \times 10^{14} \exp(-153\,000/RT) \text{ s}^{-1}$, respectively.

Most probably, the irreversible decomposition reaction competes with reversible dissociation, *i.e.*, the former occurs concurrently rather than sequentially (as the second stage after the dissociation of alkoxyamines into an active hydrocarbon radical and TEMPO). One can calculate the ratio $k_{\text{dec}}/k_1 = P_{\text{dec}} = 29 \exp(-29\,000/RT)$, which characterises the contribution of the side reaction of irreversible decomposition of alkoxyamines as a function of temperature, using the value $k_1 = 2.0 \times 10^{13} \exp(-124\,200/RT) \text{ s}^{-1}$ (Ref. 93). At 433 K, we have $P_{\text{dec}} \approx 10^{-2}$, which means that no more than 1% of the dissociating alkoxyamine molecules undergo irreversible decomposition. At first glance, this is a negligible value. However, taking into account the half-life of alkoxyamine (at this temperature $\tau_{1/2} = 0.69/k_1 \approx 0.5 \text{ min}$), we obtain that the alkoxyamine manages to enter into a reversible dissociation $\rightleftharpoons$ recombination cycle hundreds of times over the time necessary for complete conversion (several hours). Therefore, at first glance small losses of the alkoxyamine due to the irreversible decomposition in each cycle are accumulated and become comparable with its initial concentration (complete deactivation). As temperature decreases (*e.g.*, down to 393 K), the P_{dec} value becomes nearly halved; however, the $\tau_{1/2}$ value increases dramatically (by about a factor of 40) with concomitant sharp decrease in the number of reversible cycles and losses due to deactivation of the alkoxyamine.

4. Kinetics of alkoxyamine-mediated polymerisation of styrene

The kinetics of styrene polymerisation in the presence of alkoxyamines was reported in most detail by Greszta and Matyjaszewski.¹⁰⁶ The main goal of this study was to reveal key features of the process, which make it possible to infer the details of the mechanism of 'living'-chain polymerisation. A short list of the most important characteristics of 'living'-chain styrene polymerisation is presented below.

— The rate of polymerisation is proportional to the concentration of the monomer (*i.e.*, the process is first-order with respect to the monomer) and independent of the concentration of alkoxyamine (a zero order process with respect to alkoxyamine) or of the concentration of a stable nitroxyl radical (as a rule, TEMPO), if the alkoxyamine is synthesised *in situ*.

— The molecular masses of polymers increase linearly with the degree of polymerisation (conversion). This is valid until at least $M_n \approx 20\,000 - 30\,000$.

— The polydispersity of the resulting polymer, which is characterised by the M_w/M_n ratio, decreases usually with conversion and then increases at later stages of the process. The M_w/M_n value varies depending on the reaction conditions, but, as a rule, remains less than 1.3.

— Throughout the polymerisation, the concentration of the stable nitroxyl radical, as determined by ESR spectroscopy, is 0.1%–1.0% from the initial concentration of alkoxyamine (or its precursor, TEMPO) introduced into the reaction system.¹⁰⁷

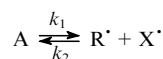
This makes it possible to draw some conclusions. The fact that the polymerisation rate, W , of the monomer is independent of the

concentrations of alkoxyamine and the stable nitroxyl radical (TEMPO) and coincides with the rate of self-initiated polymerisation of the monomer shows that self-initiation is primarily responsible for maintaining the concentration of active centres $[R]$, which, in turn, controls the polymerisation rate ($W \sim [R]$). Thus, the rate of self-initiation (W_i) (or, generally, any radical initiation) controls the polymerisation rate.

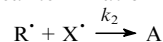
Despite the controlling effect of W_i with respect to W , alkoxyamine used as the agent for 'living' polymerisation controls almost completely the length of growing polymer chains so that they grow throughout the polymerisation process (at least, most of them do not undergo termination). This can only occur if $W_i \ll W_A$ (W_A is the dissociation rate of alkoxyamine, $W_A = k_1[A]$), *i.e.*, if each chain initiation act corresponds to many dissociation $\rightleftharpoons$ recombination acts of alkoxyamine, so that each newly initiated chain manages to be involved repeatedly in this reversible cycle.

The narrowing of molecular mass distribution of the resulting 'living' polymer down to a M_w/M_n value of 1.3 (*cf.* $M_w/M_n = 1.5 - 2.0$ for conventional radical polymerisation) also suggests the 'living' character of polymer chains. On the other hand, the increase in the M_w/M_n ratio at later stages of polymerisation indicates some side reactions.

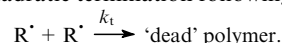
The fact that the relative concentration of a stable nitroxyl radical $X^{\bullet}$ is low ($[X]/[A] = 10^{-2} - 10^{-3}$) and changes only slightly during the time necessary for nearly complete conversion of the monomer indicates that the equilibrium constant $K = k_1/k_2$ of the following process is very low.



This equilibrium is shifted rather slowly under the action of disturbing factors (first of all, quadratic chain termination, $R^{\bullet} + R^{\bullet}$) which are developed during the polymerisation; hence, it may be always thought that $k_1[A] \approx k_2[R][X]$, where $[A] \approx [A]_0$. If K can be measured independently, then, using this value, one can assess the concentration of active centres $[R]$ over a period necessary for nearly complete conversion. For instance, the equilibrium constant of alkoxyamine-mediated 'living' polymerisation performed under standard conditions ($T = 393 \text{ K}$) is $10^{-11} \text{ mol litre}^{-1}$,¹⁰⁶ hence $[R] = k_1[A]/k_2[X] = 10^{-9} - 10^{-8} \text{ mol litre}^{-1}$. Usually, the concentration of alkoxyamine is $10^{-2} \text{ mol litre}^{-1}$ and that of the nitroxyl radical is $10^{-5} - 10^{-4} \text{ mol litre}^{-1}$. Therefore, the polymerisation process proceeds almost entirely at $[X] \gg [R]$, which provides a complete control of the reversible dissociation $\rightleftharpoons$ recombination cycle over the chain propagation, since quadratic chain termination makes a negligible contribution in this case. Actually, in the presence of dissociating alkoxyamine each growing chain undergoes either a linear termination following the mechanism



(a fictitious, temporarily termination, since the adduct A can dissociate, thus retaining the 'livingness' of the chain) or a quadratic termination following the pathway



The contribution of the latter process determines the extent to which the alkoxyamine-mediated chain propagation can be not in control. Quantitatively, the contributions of linear and quadratic termination are characterised by the probabilities α_1 and α_2 .

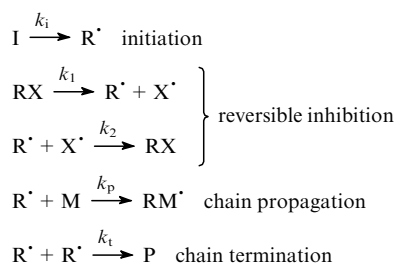
$$\alpha_1 = \frac{k_2[R][X]}{k_2[R][X] + k_t[R]^2},$$

$$\alpha_2 = \frac{k_t[R]^2}{k_2[R][X] + k_t[R]^2}.$$

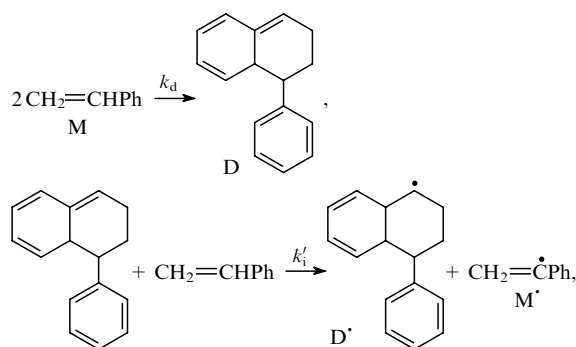
Thus, taking into account that $[X] \gg [R]$ and $k_2 \approx k_t$, we get $\alpha_1 \approx 1$ and $\alpha_2 \ll 1$.

5. Kinetics of alkoxyamine-mediated 'living' radical polymerisation

Initially, the kinetic analysis of a polymerisation process proceeding in the presence of alkoxyamines (as well as other reversible inhibitors, iniferters and other agents) was performed in the framework of rather rough approximations which oversimplified the situation under consideration. Most concisely, the mechanism of this polymerisation process is described by Scheme 1. This scheme should only be augmented with a new stage to describe the generation of active radicals upon decomposition of initiators I (organic peroxides, hydroperoxides, azonitriles, *etc.*) with the initiation rate $W_i = k_i[I]$ (Scheme 5).



For a self-initiated polymerisation of the monomer, $W_i = k_{im}[M]^n$, where n can take any value depending on the specific generation mechanism of $\text{R}^\bullet$. For styrene, this mechanism involves the reactions^{108, 109}



which proceed at 393 K with the rate constants $k_d = 3 \times 10^{-8}$ (see Refs 110 and 111) and $k_i' = 5 \times 10^{-8} \text{ litre mol}^{-1} \text{ s}^{-1}$ (see Refs 106 and 112). The n value lies between 2 and 3.

Reversible inhibition steps are the key stages of the reactions. Competitive entrapment of radical $\text{R}^\bullet$ by a stable free radical $\text{X}^\bullet$ prevents the growing chains $\text{R}^\bullet$ from being terminated quadratically. During the time interval between acts of chain initiation (or regeneration) the radicals $\text{R}^\bullet$ manage to react with the monomer, thus extending the polymer chain.

It is an easy matter to perform the kinetic analysis of such a polymerisation scheme (Scheme 5). In the steady-state approximation, the polymerisation rate W is calculated as follows

$$W = k_p[M] \left(\frac{W_i}{k_t} \right)^{1/2} \quad (19)$$

This expression for W is the same as that used to describe a conventional radical polymerisation without reversible inhibition. This result is obvious. Indeed in the steady state the reversible inhibition reactions responsible for 'living' polymerisation make no contribution to the stationary concentration of growing polymer chains $[\text{R}]_s$ (and, correspondingly, to the W value), since all radicals $\text{R}^\bullet$ and $\text{X}^\bullet$ generated in the stage $\text{RX} \rightarrow \text{R}^\bullet + \text{X}^\bullet$ leave the reaction system by the stage $\text{R}^\bullet + \text{X}^\bullet \rightarrow \text{RX}$. Therefore, if the time necessary for establishment of a steady state in the polymerisation system (τ_s) is much shorter than that necessary for complete conversion (t), the alkoxyamine present in the system has no effect on the polymerisation kinetics from the moment

$\tau_s \ll t$ onwards, *i.e.*, nearly from the beginning of the polymerisation process.

However, the chain propagation regime in the presence of alkoxyamine differs fundamentally from that in conventional radical polymerisation. Actually, in the latter case the average integrated chain length (v) at instant t is given by the following expression

$$v = \frac{\int_0^t W dt}{\int_0^t W_i dt} \quad (20)$$

where $\int_0^t W dt$ is the total number of monomer units in the chains and $\int_0^t W_i dt$ is the total number of the initiated chains. In a

particular case, for $W \simeq \text{const}$ and $W_i \simeq \text{const}$, we get $v \simeq W/W_i \simeq \text{const}$. On the other hand, for 'living' polymerisation the average integrated chain length (v_x) at instant t will be determined by the total number of 'dead' and 'living' chains accumulated by the instant t

$$v_x = \frac{\int_0^t W dt}{\int_0^t W_i dt + [\text{RX}]_t} \quad (21)$$

where $[\text{RX}]_t$ is the stationary (quasi-stationary) concentration of alkoxyamine at instant t , which in turn is equal to the concentration of 'living' chains.

'Living'-chain polymerisation proceeds if $\int_0^t W_i dt \ll [\text{RX}]_t$. In this case, the v_x value is calculated by the formula

$$v_x \simeq \frac{\int_0^t W dt}{[\text{RX}]_t} \simeq \frac{\Gamma}{[\text{RX}]_t} \quad (22)$$

Here, $[\text{RX}]_t \simeq \text{const}$; if an iminoxyl is used as alkoxyamine, then $k_1/k_2 \ll 1$ and $[\text{RX}]_t \simeq [\text{RX}]_0$. Unlike conventional radical polymerisation in which the chain length remains virtually unchanged throughout the process [Eqn (20)], 'living' polymerisation in the presence of alkoxyamine is characterised by linear increase in v_x with the degree of conversion Γ [Eqn (22)] provided that the overall concentration of chains generated by the initiator throughout the polymerisation process is much lower than the equilibrium (initial) concentration of the additive RX .

These are the results of the simplest and obvious analysis of the steady-state 'living'-chain polymerisation process described by Scheme 5. It should be noted that in the absence of additional initiation the system cannot reach the steady state and the analysis is complicated.

Theoretical studies on the mechanism of 'living' radical polymerisation can be divided into two groups.

1. Early studies^{5, 113} aimed at revealing salient features of the mechanism responsible for the transformation of usual radical polymerisation into 'living' polymerisation.

2. More recent studies^{88, 106, 114–118} on the kinetic analysis of the polymerisation mechanism and molecular mass distributions of polymeric products formed in the system carried out with the use of supercomputers and sophisticated mathematical procedures. Obviously, the mechanism presented in Scheme 5 is unsuitable for analysing the molecular mass distributions (MMD). To this end, Scheme 5 should be augmented with equations for chains of different length containing v ($v = 1, 2, \dots$) monomer units instead of the equations for a growing chain of an infinite length, while the chain propagation reaction should be written as a sequence of v stages. Reversible inhibition and quadratic termination reactions should also be divided into a variety of identical

stages in which reagents R of different chain length are involved. The chain length effect of the reagent R on the rate constants can be ignored by assuming that they are the same for identical reactions. However, the number of differential equations to be integrated numerically increases by two orders of magnitude and more (instead of 5 equations shown in Scheme 5) even if the analysis is restricted to not very long chains. Calculations of MMD for the chains up to 500 monomer units long ($v = 500$) have been reported,¹¹⁵ as well as some artificial simplifying procedures (introduction of special subsystems and 'closure reactions').¹¹³

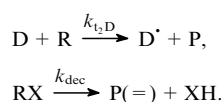
Let us consider the results obtained in three theoretical studies^{88, 106, 114} in which the results of calculations were compared in detail with the latest experimental results.

Computer simulation¹⁰⁶ of a process described by Scheme 5 for M = styrene and X = TEMPO was performed using the PREDICI programme package.^{119–121} The numerical values of the rate constants and concentrations of reagents (for 393 K) are listed below.

Parameter	Numerical value	Ref.
Rate constants of reactions/litre mol ⁻¹ s ⁻¹		
k_p	2000	102, 122
k_d	3×10^{-8}	110, 111
k'_i	5×10^{-8}	112
k_t	10^7	123, 124
Concentration/mol litre ⁻¹		
[M]	10	106
[RX]	10^{-2}	106

Unlike the values of rate constants k_p , k_d , k'_i and k_t , the values of k_1 , k_2 and some other rate constants were attenuated in the course of computer simulation because of a wide scatter of the data reported in different publications.

According to calculations,¹⁰⁶ Scheme 5 adequately describes all experimentally observed characteristic features of the process (see previous Section) assuming that $K = k_1/k_2 \leq 10^{-10}$ mol litre⁻¹. Based on detailed quantitative comparison of calculated and experimental dependences of the polydispersity index, M_w/M_n , on the degree of polymerisation, the values of the constants k_1 and k_2 were refined to be $K \simeq 10^{-11}$ mol litre⁻¹; $k_1 = 8 \times 10^{-4}$ s⁻¹ and $k_2 = 8 \times 10^7$ litre mol⁻¹ s⁻¹. This also made it possible to augment Scheme 5 with new stages necessary for improving the agreement between calculated and experimental data.



Here, P(=) is the polymer with a double bond in the end group, XH is hydroxylamine, $k_{t,D} = 50$ litre mol⁻¹ s⁻¹ is the rate constant of chain transfer to dimer D formed in the self-polymerisation of the monomer (see above), k_{dec} is the rate constant of dissociation reaction accompanied by hydride transfer and $k_{dec} \simeq 10^{-5}$ s⁻¹ (see Ref. 104).

These calculations have also confirmed that the reactions shown in Scheme 5 satisfy the principle of stationary concentrations. Using the above-mentioned values of rate constants, concentrations and temperature, the steady state is reached at a degree of polymerisation of less than 1%, i.e., nearly from the beginning of the polymerisation process. The calculated stationary concentrations of growing chains [R] and stable iminoxyl radical [X] were found to be 10^{-8} and 10^{-5} mol litre⁻¹, respectively.

Similar results have also been obtained¹¹⁴ for the same styrene–TEMPO reaction system using another type of computational procedure (the Monte Carlo stochastic algorithm^{125–128}). This makes it possible to perform calculations without recourse to supercomputers. The results of calculations for $T = 393$ K were supplemented with those obtained for $T = 363$ K¹¹⁴ which were then compared with the experimental results obtained at the same

temperature.⁷⁸ The parameters listed below provided the best fit between the calculated and experimental data.

Parameter	Numerical value
Concentration/mol litre ⁻¹	
[M]	8.75
[RX]	$3.7 \times 10^{-3} - 4.4 \times 10^{-2}$
Rate constants of reactions	
k_1/s^{-1}	2.5×10^{-3}
$k_2/\text{litre mol}^{-1} s^{-1}$	2.5×10^8
$k_p/\text{litre mol}^{-1} s^{-1}$	950
$k_t/\text{litre mol}^{-1} s^{-1}$	10^7
$k_d/\text{litre mol}^{-1} s^{-1}$	1.5×10^{-9}
$k'_i/\text{litre mol}^{-1} s^{-1}$	4.5×10^{-9}
k_{dec}/s^{-1}	8×10^{-6}

The polydispersity indices, M_w/M_n , obtained analytically^{90, 129} and found from simulation have also been compared.¹¹⁴

The M_w/M_n ratio was calculated using the formula

$$\frac{M_w}{M_n} = \frac{1}{\gamma x} + \frac{1}{x} \left[2 + \frac{(\beta - 1)(2 - x)}{\alpha - \beta} \right] - \frac{2\alpha(1 - \alpha)}{(\beta^2 - \alpha^2)x^2} \left[1 - (1 - x)^{\frac{1+\beta}{\alpha}} \right], \quad (23)$$

where x is the degree of monomer conversion, $\gamma = [M]_0/[RX]$, $\alpha = [R]/[RX]$ and $\beta = k_2[X]/k_p[RX]$. It was found that the results of computer simulation fit well the theoretical curve.

Fischer⁸⁸ reported the most detailed computer simulation. He analysed two types of 'living'-chain polymerisation, without additional initiation (Scheme 1) and with varied intensity of initiation in order to establish the range of the effect of the initiation on polydispersity M_w/M_n (Scheme 5). Different versions of syntheses of the adducts RX were also considered, including the synthesis *in situ* and those with different dynamics of reversibility (this was achieved by varying the constants k_1 and k_2 over a wide range).

The first case (see Scheme 1) corresponds to a non-steady-state process. For very short times, $t \ll [k_1^2(k_t[RX]_0/k_1 - 1)]^{-1/2} \simeq (k_1 k_t [RX]_0)^{-1/2}$, the following relation is valid

$$[R] = [X] = k_1[RX]_0 t. \quad (24)$$

For the time interval $(k_1 k_t [RX]_0/3)^{-1/2} \ll t \ll k_t [RX]_0/24k_1^2$, which covers almost entirely the range of practically significant t values, one obtains

$$[R] = [RX]_0 \left[\frac{k_1}{3(k_t[RX]_0)^2 t} \right]^{1/3},$$

$$[X] = [RX]_0 \left(\frac{3k_1^2 t}{k_t[RX]_0} \right)^{1/3},$$

$$[RX] = [RX]_0 - [X] \simeq [RX]_0,$$

$$[P] = [X] - [R] \simeq [X], \quad (25)$$

$$[M] = [M]_0 \exp \left\{ -\frac{3}{2} k_p [RX]_0 \left[\frac{k_1 t^2}{3(k_t[RX]_0)^2} \right]^{1/3} \right\}.$$

For very long times, $t \gg 2k_t[RX]_0/k_1^2$, the concentrations vary as follows:

$$[R] = \frac{[RX]_0}{k_1 t},$$

$$[X] = [RX]_0 \left(1 - \frac{k_t [RX]_0}{k_1^2 t} \right) \simeq [RX]_0, \quad (26)$$

$$[RX] = \frac{[RX]_0^2 k_t}{k_1^2 t},$$

$$[P] = [X] - [R] \simeq [X] \simeq [RX]_0.$$

Expressions (24)–(26) were derived assuming equal values of the constants k_2 and k_t in Scheme 1 ($k_2 \equiv k_t$). Successful applicability of relationships (25) throughout the polymerisation process (from $t_0 \approx 10^2$ to $t_f \approx 10^4$ s),[¶] for a conventional $[\text{RX}]_0$ value of about 10^{-2} mol litre⁻¹ requires that the condition $k_1 \ll 2 \text{ s}^{-1}$ (or 0.7 s^{-1}), depending on the choice of k_t value, 10^8 or 10^7 litre mol⁻¹ s⁻¹, be met. Since the k_1 values for alkoxyamines used in 'living' polymerisation do not exceed 10^{-2} s^{-1} at the operating temperatures, the conditions for the upper (t_f) and lower (t_0) bounds of the time interval are always met.

Using analytical expressions (24)–(26), one can assess the time taken to reach the maximum concentration of growing polymer chains $[\text{R}]_{\text{max}}$. We have $t_{\text{max}} = (2k_1k_t[\text{RX}]_0)^{-1/2} \approx 0.02 \text{ s}$ for $k_1 = 10^{-2} \text{ s}^{-1}$, $k_t = 10^7$ litre mol⁻¹ s⁻¹ and $[\text{RX}]_0 = 10^{-2}$ mol litre⁻¹. Substituting this value into Eqn (24) gives $[\text{R}]_{\text{max}} \approx 2 \times 10^{-6}$ mol litre⁻¹.

No practical implementation of the polymerisation mechanism described by Scheme 1 has been reported so far. This is due to self-initiation observed for those monomers which can undergo alkoxyamine-mediated 'living' polymerisation, such as styrene and several its derivatives, or mixtures of styrene with other monomers. Therefore it is reasonable to use the analytical solution of Eqns (24)–(26) for establishing the mechanism of the action of alkoxyamines (as well as any other agents which can reversibly accept growing polymer chains) as agents for 'living' polymerisation.

In particular, it seems to be very convenient to use expression (25) for the determination of the constant k_1 (in combination with k_t) of alkoxyamines from the data on the kinetics of the accumulation of X, which can be obtained from ESR measurements. Obviously, the corresponding experiments should be carried out using such solvents in which no self-initiation is developed in the temperature range chosen (the use of styrene and its derivatives is of course impermissible). For inert solvents, the absence of chain propagation step is of no significance since it is not considered in deriving Eqn (25).

For Scheme 1, analysis of MMD leads to the following interesting results. The contribution of quadratic chain termination ($\text{R}^* + \text{R}^* \rightarrow \text{P}$), which produces 'dead' chains and broadens the MMD, can be reduced to the extent that the value M_w/M_n will approach unity to the second decimal place. The conditions for minimisation are governed by the constant k_1 . Assuming that the k_1 value for $[\text{RX}] = 10^{-2}$ mol litre⁻¹ varies between 3×10^{-3} and $3 \times 10^{-2} \text{ s}^{-1}$ and taking $k_p = 2000$ litre mol⁻¹ s⁻¹, $k_t = 2.5 \times 10^{-8}$ litre mol⁻¹ s⁻¹ and $[\text{M}] = 10$ mol litre⁻¹, we find that the ratio M_w/M_n lies in the range 1.01–1.03. As k_1 increases by one and two orders of magnitude, the polydispersity, M_w/M_n , increases to 1.107 (for $k_1 = 3 \times 10^{-1} \text{ s}^{-1}$) and 1.412 (for $k_1 = 3 \text{ s}^{-1}$), respectively. However, it should be noted that no k_1 values meeting the condition $k_1 \geq 10^{-1} \text{ s}^{-1}$ have been reported for alkoxyamines, so they seem to be unrealistic.

Varying the $[\text{RX}]$ value at a given k_1 ($k_1 = 10^{-2} \text{ s}^{-1}$) has virtually no effect on the polydispersity, that is, the M_w/M_n ratio decreases by about 0.01 as $[\text{RX}]$ increases by a factor of 30 (from 3×10^{-3} to 10^{-1} mol litre⁻¹).

All the above-mentioned values of the ratio M_w/M_n were obtained for 90% conversion (Γ). The dependence of the polydispersity index, M_w/M_n , on Γ is determined by the numerical values of k_1 and $[\text{RX}]$. For small k_1 and high $[\text{RX}]$, the polydispersity is high in the early stages of polymerisation and then it decreases as Γ increases. For instance, calculations with $k_1 = 10^{-2} \text{ s}^{-1}$ and $[\text{RX}] = 10^{-1}$ mol litre⁻¹ show that the M_w/M_n ratio varies from 1.308 for $\Gamma = 5\%$ to 1.026 for $\Gamma = 50\%$ and reaches 1.017 for $\Gamma = 90\%$. On the contrary, for large k_1 the polydispersity increases as Γ increases. According to calculations with $k_1 = 3 \text{ s}^{-1}$ and $[\text{RX}] = 10^{-2}$ mol litre⁻¹, the

M_w/M_n ratio is 1.079, 1.256 and 1.412 for $\Gamma = 5\%$, 50% and 90%, respectively.

The results of calculations make it possible to predict the efficiency of the use of adducts RX as agents for 'living' polymerisation. Actually, the early stages of the polymerisation process (at times t not too long compared with t_{max}) are characterised by comparable concentrations of growing polymer chains R^* and scavengers X^* (both of them are products of dissociation of the adducts RX) and by a large contribution of 'dead' polymer (the product of quadratic chain termination). Correspondingly, the polydispersity is also high ($M_w/M_n \rightarrow 1.5\text{--}2.0$). As $[\text{R}]$ decreases and $[\text{X}]$ increases, both the contribution of 'dead' polymer and the polydispersity decrease. The rate of the decrease is governed by the constant k_1 since both the decrease in $[\text{R}]$ and the corresponding increase in $[\text{X}]$ are due to the irreversible consumption of radicals R^* in the reaction of quadratic chain termination $\text{R}^* + \text{R}^* \rightarrow \text{P}$, which is responsible for the shift of the dissociation equilibrium toward the formation of X. Therefore, an increase in the number of dissociation $\rightleftharpoons$ recombination cycles per unit time (*i.e.*, an increase in the k_1 constant) leads to accelerated accumulation of X (and to a decrease in $[\text{R}]$). In turn, a decrease in $[\text{R}]$ and an increase in $[\text{X}]$ lead to a decrease in the amount of 'dead' polymer produced in the reaction $\text{R}^* + \text{R}^* \rightarrow \text{P}$ and to an increase in the fraction of the polymer produced by 'living' polymerisation, $\text{R}^* + \text{X}^* \rightarrow \text{PX}$. Correspondingly, the polydispersity will decrease from values corresponding to large contributions of 'dead' polymer (1.5–2.0) to those typical of 'living'-chain polymerisation (~ 1.0).

However, in parallel with the positive effect (shortening of the time interval necessary for passage from the early stages of the process with large contribution of 'dead' polymer to the stage in which this contribution is small) there is also a negative effect of high k_1 values. For large constants k_1 , the contribution of 'dead' polymer increases since the reaction of permanent chain termination, $\text{R}^* + \text{R}^* \rightarrow \text{P}$, is of higher order with respect to $[\text{R}]$ than the reaction of temporary chain termination, $\text{R}^* + \text{X}^* \rightarrow \text{PX}$. In addition, for too high k_1 values, the polydispersity will increase with increase in the degree of polymerisation. Therefore it is necessary to find an optimum k_1 value. The limits for the optimum range of k_1 values can be evaluated using the results obtained by Fischer.⁸⁸

The results of calculations for a polymerisation process described by Scheme 5 which includes an additional initiation stage have also been reported.⁸⁸ Both self-initiation (for styrene, this is a termolecular initiation with the rate constant $k_s = 2 \times 10^{-10}$) and initiation using a conventional radical initiator (a unimolecular initiation with the rate constant $k_i = 5 \times 10^{-3} \text{ s}^{-1}$, the initiator concentration $[\text{I}] = 4 \times 10^{-2}$ mol litre⁻¹) were considered. These results were obtained by computer simulation rather than using analytical methods.

The numerical estimate of the time t_s necessary for establishment of the steady state in the reaction system is one of the most important results reported by Fischer.⁸⁸ Unlike conventional radical polymerisation with $t_s < 1 \text{ s}$, in the presence of RX the t_s value increases substantially and reaches 10^2 to 10^4 s depending on the ratio between the initiation rate of chain propagation reaction and the dissociation rate of RX. This numerical estimate shows that under certain conditions the steady-state approximation can actually be used to analyse Scheme 5.

Of great importance is also the establishment of the fact that the polymerisation rate and the polydispersity of the resulting polymer depend on the initiation rate in a different manner. As the initiation rate W_i increases, under certain conditions the polymerisation rate W increases faster than the polydispersity index M_w/M_n . Because of this, the polymerisation can be accelerated substantially with virtually no increase in the M_w/M_n ratio. Calculations for styrene ($T = 393 \text{ K}$, $k_p = 2000$, $k_t = 2.5 \times 10^8$ litre mol⁻¹ s⁻¹) with $[\text{RX}] = 10^{-2}$ mol litre⁻¹ ($k_1 = 10^{-2} \text{ s}^{-1}$) show that without initiation ($W_i = 0$) the time necessary for 90% conversion is 165 h and the M_w/M_n ratio equals 1.017. For the initiation rate $W_i = 2 \times 10^{-4}$ mol litre⁻¹ s⁻¹,

[¶] In this case, the upper (t_f) and lower (t_0) bounds for the time interval meet the conditions $t_f \ll k_t[\text{RX}]_0/24k_1^2$ and $t_0 \gg (k_1k_t[\text{RX}]_0/3)^{-1/2}$, respectively.

the average polymerisation rate is nearly doubled so that a 90% conversion is reached after 81 h, the polydispersity of the polymer being very low ($M_w/M_n = 1.04$).

Summing up the results of theoretical studies,^{88, 106, 114} one can draw the following conclusions.

'Living' radical polymerisation in the presence of alkoxyamines (either supplied 'as is' from an external source or synthesised *in situ*) follows the mechanism shown in Scheme 1 with no additional initiation. The initiation is due to reversible dissociation ($RX \rightleftharpoons R^\bullet + X^\bullet$) only. Here, we are concerned with the transformation of a usual radical polymerisation into 'living' polymerisation owing to conversion of a short-lived chain carrier R ($\tau < 1 \text{ s} \ll t$, where t is the time necessary for complete conversion) into a long-lived one ($\tau > t \approx 10^4 \text{ s}$).

The process which includes only the stages shown in Scheme 1 is an 'ideal' process as regards the polydispersity of the resulting polymer. That is, at particular $K = k_1/k_2$ values characteristic of the known alkoxyamines and constants k_p and k_t typical of the known monomers there is a temperature range suitable for performing a polymerisation to yield a virtually 'monodisperse' product ($M_w/M_n = 1.0$). However, this mechanism is impracticable.

The real mechanism is described by Scheme 5. This is characterised by a higher polymerisation rate as compared to the rate of the process described by Scheme 1. If the rates of the initiation reactions, $I \rightarrow R^\bullet$ and $RX \rightarrow R^\bullet + X^\bullet$, lie within particular limits, the polymerisation process leads to nearly the same 'monodisperse' product ($M_w/M_n = 1.0$) as that obtained in the 'ideal' case (see Scheme 1).

Comparison of calculated and experimental results shows that the mechanism presented in Scheme 5 adequately describes all experimentally observed characteristic features of 'living'-chain radical polymerisation (see previous Section), except for specific details of the evolution of the polydispersity (M_w/M_n) at deep stages of polymerisation. Rigorous quantitative description of these details was performed in the framework of a sophisticated mechanism augmented with side disproportionation reactions (see above).

Comparison of calculated and experimental results was also used for the evaluation of the numerical values of the reported (or measured independently) rate constants k_i , k_1 , k_2 , k_p , k_t , k_{tD} and k_{dec} for the styrene-TEMPO reaction system. If the difference between the known K values exceeded an order of magnitude, their values were corrected and the most plausible K were used.

Thus, the results of thorough quantitative studies^{88, 106, 114} of the polymerisation processes proceeding in the presence of alkoxyamines or other compounds possessing similar properties can serve as a theoretical basis for designing various 'living' polymerisation processes because these have made it possible to find correlations between the reaction parameters (temperature and the concentrations of reagents) and the properties of agents for 'living' polymerisation (the values of the constants k_1 and k_2 at a given temperature). On the other hand, these results can be used for choosing optimum reaction conditions for conducting a polymerisation process in the styrene-TEMPO reaction system instead of performing labour-consuming experiments on 'adjusting' technological details of the process.

Very recently, ESR studies of the mechanism of 'living' polymerisation of styrene in the presence of alkoxyamines (a styrene-dibenzoyl peroxide-TEMPO system with alkoxyamine synthesised *in situ*) revealed^{99, 100} the appearance of a doublet ESR spectrum of a system under study at medium degrees of conversion instead of the conventional singlet ESR spectrum of TEMPO. The additional component was attributed to an iminoxyl of unknown nature (we will denote it as $X^\bullet$). The same phenomenon was also observed^{85, 130, 131} in studies of the polymerisation of styrene in the presence of alkoxyamine preliminarily synthesised from styrene and TEMPO.

The ESR spectrum of the 'additional' iminoxyl $X^\bullet$ is characterised by broader lines and a smaller hyperfine coupling constant $a_N = 13.6 \text{ G}$, whereas for 'normal' TEMPO $a_N = 15.6 \text{ G}$. This

substantial change in the parameters of the ESR spectrum indicates essential changes in the nature of the substituents at the 'O-N group. Appreciable decrease in a_N accompanied by broadening of spectral lines could, *e.g.*, be observed if $X^\bullet$ contains the phenyl substituent [then the a_N value should lie between 12.1 and 13.5 G (see Ref. 132)]. This is also indicated by the fact that the 'additional' iminoxyl $X^\bullet$ is observed only if styrene is used as monomer. Neither the chemical mechanism of the formation of $X^\bullet$ nor the role it plays in the polymerisation process have been established so far. Probably, $X^\bullet$ is not involved in the reversible dissociation $\rightleftharpoons$ recombination cycle and the accumulation of $X^\bullet$ merely increases⁸⁵ the overall concentration of iminoxyls. However, it is even more probable that $X^\bullet$ does participate in the reactions of the reversible cycle and forms an adduct $RX^\bullet$ which is characterised by higher equilibrium constant $K' = k'_1/k'_2$ than that of RX adduct.

Finally, experimental results obtained by Boutevin and Bertin¹³³ differ substantially from the calculated data obtained using the extended Scheme 5. The reasons for such discrepancies have also been discussed.¹³³

6. Extension of the area of application of alkoxyamines. Copolymerisation of styrene and its derivatives with other monomers

Alkoxyamines appeared to be efficient agents for 'living' radical polymerisation only of such monomers as styrene and its derivatives (4-hydroxy-, 4-acetoxystyrenes,⁶⁹ 4-bromostyrene,⁷⁰ 3- and 4-chloromethylstyrene,⁷¹ 4-ethyl-4'-vinylbiphenyl, 1,4-divinylbenzene,⁷⁴ *etc.*). Numerous attempts^{61, 73-78} to perform 'living' polymerisations of other monomers (acrylates, methacrylates, vinyl acetate, *etc.*) in the presence of alkoxyamines either failed or were of little value, resulting in low yields and very low molecular masses of polymers. Synthesis of polyacrylates based on *n*-butyl acrylate and other monomers at 428 K in the presence of hydroxy-substituted TEMPO (4-HO-TEMPO) was the most successful, the polymers were obtained with $M_n = 10\,500 - 27\,000$ and $M_w/M_n \geq 1.53$.⁷³

The most plausible reason for unsuccessful polymerisations is that, unlike styrene and its derivatives, the molecules of the above-mentioned monomers have no phenyl substituent which affects the strength of the C-ON bond in RX subject to reversible dissociation (see Section IV). The aromatic ring is known⁸⁴ to be responsible for the redistribution of the electron density in the vicinity of the nearest covalent bond in such a manner that this bond is weakened and the corresponding binding energy decreases by several tens of kJ. However, the C-ON bond in alkoxyamines RX based on (meth)acrylates and related monomers is too strong. Because of this, the attainment of a dissociation rate of this bond suitable for performing a 'living' polymerisation requires elevated temperatures. This may change the dissociation mechanism from a reversible process with the formation of $R^\bullet$ and $X^\bullet$ to irreversible transformation of RX into $R(=)$ and hydroxylamine, XH . Possibly, this is the reason why polymerisations of acrylates at elevated temperature (428 K instead of 383-403 K for styrene) were, in general, unsuccessful.⁷⁵

The ability of (meth)acrylates and related monomers to undergo 'living' polymerisation following the mechanism shown in Scheme 5, *i.e.*, by extending the polymer chains $R^\bullet$ at the instant of their release from adducts RX ($R^\bullet + M \rightarrow RM^\bullet$) is beyond question. This is supported by, *e.g.*, the possibility of producing block copolymers of styrene with (meth)acrylates by two-step polymerisation.⁷⁸ The first stage of the process is 'living' polymerisation of styrene in the presence of alkoxyamine until complete consumption of the monomer to give poly(styryloxyamine) RX (the polystyrene chains R capped with the end group X). The second stage is copolymerisation of poly(styryloxyamine) with a new monomer, *viz.*, (meth)acrylate. This stage is performed at the same or higher temperature. As a result, one obtains not only polystyrene, but also a rather large amount of poly[styrene-*b*-(meth)acrylate] block copolymer, which indicates that the second

stage of the synthesis proceeds at least in part as a 'living' polymerisation. The addition of a mixture of (meth)acrylate with styrene instead of neat (meth)acrylate in the second stage increases the yield of the block copolymer, which reaches $\sim 100\%$ at high styrene content in the mixture. In this case, the second block of the block copolymer is a poly[styrene-*co*-(meth)acrylate] random (statistical) copolymer.^{60, 89–91, 95, 134–140}

The effect of styrene additives to (meth)acrylates introduced in order to improve the efficiency of alkoxyamines as agents for 'living' polymerisation has been studied in detail.^{78, 79, 85} It was found that a nearly 'living' polymerisation can be implemented at a sufficiently high content of styrene in the mixture. In particular, it was shown⁷⁹ that the double bonds of methacrylates are involved in 'living' polymerisation controlled by alkoxyamines if the content of styrene was 50 mol.% and more. This result is nontrivial and not obvious. Actually, consideration of reversible dissociation $\rightleftharpoons$ recombination, $RX \rightleftharpoons R^{\cdot} + X^{\cdot}$, as a process which proceeds with involvement of only those polymer chains which bear the styrene unit as the end group at the instant of recombination, $R^{\cdot} + X^{\cdot}$, suggests very fast extinguishment of 'living' polymerisation. This is associated with the fact that both copolymerisation constants, r_1 and r_2 , for the methacrylate–styrene system are less than unity ($r_1 \simeq 0.45$ and $r_2 \simeq 0.55$).¹⁴¹ Close values of r_1 and r_2 result in distinct alternation of the styrene and methacrylate units, so they have nearly equal probabilities of being the end group at the instant of recombination. If the assumption that the aromatic substituent affects the strength of the C–ON bond in RX subject to dissociation (henceforth, R_M and R_S denote the chain with the methacrylate and styrene end group, respectively) is valid, nearly half of the polymer chains will return to the initial state RX in the form of inactive adducts R_MX after each dissociation $\rightleftharpoons$ recombination cycle, thus resulting in fast extinguishment of 'living' polymerisation.

The time τ_d taken for complete deactivation ($R_SX \rightarrow R_MX$) of alkoxyamine R_SX introduced into the methacrylate–styrene mixture can be assessed from the repetition frequency of dissociation $\rightleftharpoons$ recombination cycles determined by the value of the constant k_1 . For $k_1 = 10^{-3} - 10^{-2} \text{ s}^{-1}$, we get $\tau_d \leq t \simeq 10^4 \text{ s}$, where t is the time necessary for complete conversion. Actually, during the time interval nearly equal to three half-lives of R_SX ($\tau = 3 \times 0.69/k_1 = 2 \times 10^2 - 2 \times 10^3 \text{ s}$), almost all molecules of the initial adduct R_SX are, on the average, involved in the dissociation act and nearly half of them are deactivated in the form of R_MX . When this cycle is repeated many times, the concentration of R_SX will decrease by a factor of 2^n (n is the number of cycles) compared to the initial value, $[R_SX]_0$. For instance, for $n = 3$ the $[R_SX]$ value will decrease by a factor of 8, which is adequate for nearly complete deactivation of alkoxyamine as agent for 'living' polymerisation. Then, $\tau_d \simeq 3\tau = 6 \times 10^2 - 6 \times 10^3 \text{ s}$, which means that deactivation occurs far before complete polymerisation.

This suggests that if complete conversion t takes $\simeq 10^4 \text{ s}$, then copolymerisations of methacrylates with styrene in the presence of alkoxyamines at monomer ratios close to equimolar ones will proceed as 'living' polymerisations only in the initial stages of the processes. Then, the polymerisation process either undergoes transformation into conventional radical polymerisation (if the initiation rate, W_i , is sufficiently high) or is extinguished (if W_i is too low) because of the deactivation of the initial adduct R_SX . The absence of experimental data on such an evolution⁷⁹ was explained as follows.⁸⁰ It was assumed that not only the end group, but also the penultimate unit of the polymer chain affects the strength of the C–ON bond. If so, the aromatic ring substantially weakens this bond even if it is separated by the methacrylate unit and the adduct R_MX is not completely deactivated. Because of partial deactivation of R_MX , the rate constant for dissociation, k_d , remains rather high.

Copolymerisation of styrene with acrylates in the presence of TEMPO has been studied taking butyl acrylate as an example.¹⁰¹ Here, both copolymerisation constants, r_1 and r_2 , also are less than unity, but their values differ substantially ($r_1 = 0.15$ and

$r_2 = 0.76$; M_1 is butyl acrylate and M_2 is styrene). This indicates that growing chains react mainly with the styrene rather than acrylate molecules. For acrylates, the deactivation frequency of the adducts R_SX in each dissociation $\rightleftharpoons$ recombination cycle is lower than for methacrylates. Probably, that is why the results obtained for acrylates^{82, 83, 101, 142} were encouraging. It was shown¹⁰¹ that copolymerisation of styrene with butyl acrylate at 393 K with a styrene:butyl acrylate ratio of 77:23 (azeotrope) and $[\text{TEMPO}] = 6 \times 10^{-3} \text{ mol litre}^{-1}$ exhibits distinct indications of a 'living' process. The M_n value increases as the degree of conversion increases. The best polydispersity index $M_w/M_n = 1.29$ (at $\Gamma = 65\%$ and $M_n = 59\,100$) differs appreciably from that typical of conventional radical polymerisation, while the process, according to ESR data, proceeds at a nearly stationary concentration of free iminoxyl, $[X] = (1.7 - 2.6) \times 10^{-5} \text{ mol litre}^{-1}$ (at least in the range $20\% < \Gamma < 45\%$). Considering the concentration $[X]$ and the polymerisation rate W in the 'steady-state' stage of polymerisation, one can evaluate the equilibrium constant, $K = k_1/k_2 = W[X]/k_p[M][X]_0$ ($[M]$ is the overall running concentration of both monomers, $k_p = 2040 \text{ litre mol}^{-1} \text{ s}^{-1}$).¹⁰¹ If $20\% < \Gamma < 45\%$, the $K \times 10^{11}$ value varies between 2.7(1.8) and 3.7(3.4) mol litre^{-1} (the data obtained in the experiments with the alkoxyamine synthesised *in situ* are given in parentheses). For the homopolymerisation of styrene under the same conditions, the K value reported by investigators from the same research group was found to be equal to $K = (1.50 \pm 0.3) \times 10^{-11} \text{ mol litre}^{-1}$.⁹⁹

It is believed¹⁰¹ that the observed decrease in K values during the copolymerisation is due to the deactivation of the adduct R_SX because of the substitution of the acrylate end group in R for the styrene end group. This assumption is confirmed by an increase in the polydispersity index at deep stages of the process ($M_w/M_n = 1.5\% - 1.7\%$ for 80% conversion). This also seems to be the reason why the M_n value increases nonlinearly with conversion and goes beyond the limits for $\Gamma > 70\%$. Unsuccessful attempts to perform homopolymerisation of acrylate under analogous conditions also indirectly confirm that R_SX is deactivated.

A procedure for improving the efficiency of 'living' polymerisation of dimethacrylate in the presence of alkoxyamines by performing its copolymerisation with styrene under conditions of three-dimensional radical polymerisation has been reported.¹⁴³ This includes the addition of a two- or threefold excess of styrene to the network-forming monomer (dimethacrylate) in order to perform a 'living' copolymerisation. It is essential that the number of cross-links per unit volume in the polymer network, ν , in the copolymer decreases only slightly compared to the homopolymers of dimethacrylate. The point is that, because of cyclisation in the macromolecules of homopolymers,^{144–146} the effective ν value is much smaller than the 'nominal' one, so copolymerisation of dimethacrylate with monomers which cannot form polymer networks (e.g., styrene) and contain only one double bond in the molecule increases the effective ν value.

To sum up, we can say that copolymerisation of (meth)acrylates and related monomers with styrene appears to be quite an efficient procedure for extending the area of application of alkoxyamines as agents for 'living' polymerisation.

7. Synthesis of block copolymers in the presence of alkoxyamines

A trivial method for the synthesis of block copolymers by 'living'-chain polymerisation includes two stages. The first stage is 'living'-chain polymerisation of the first monomer (M_1) to give a homopolymer with the desired molecular mass M_n and the lowest polydispersity (ideally, $M_w/M_n = 1.0$, block A). The second stage involves the extension of 'living' chains grown in the first stage with the other monomer (M_2) to give the second block (also with controlled M_n and M_w/M_n values, block B). Obviously, this approach can only be used if the 'living' end group of the chain A can initiate 'living' polymerisation of M_2 . Taking into account the limitations on the activity of alkoxyamines as agents for 'living'

polymerisation (see above), this procedure allows only the synthesis of AB block copolymers based on styrene and its derivatives. Usually, polystyrene is used as the block A while a homopolymer of a substituted styrene is used as the block B, or *vice versa*.

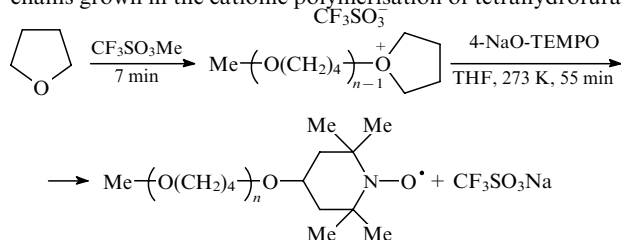
Synthesis of an AB block copolymer with 'living' poly(*p*-bromostyrene) as the block A and polystyrene as the block B has been described.⁷⁰ Block A was obtained by polymerisation of *p*-bromostyrene in the presence of 4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy and dibenzoyl peroxide. 'Living' poly(*p*-bromostyrene) thus obtained was used in the second stage to perform 'living' polymerisation of styrene (block B). The overall process resulted in the preparation of the AB block copolymer.

Yet another block copolymer was synthesised, with the homopolymer of 3- and 4-chloromethylstyrene (a mixture of isomers in a 2:1 ratio) as the block A and polystyrene as the block B.⁷¹ Alkoxyamine was synthesised *in situ* from TEMPO and dibenzoyl peroxide in the bulk of 3(4)-chloromethylstyrene.

Blocks A and B can be synthesised not only from homopolymers, but also from copolymers with a rather high content of styrene or its derivatives (in order to ensure high efficiency of alkoxyamines as agents for 'living' polymerisation).^{51, 55, 73, 76, 79, 140, 147–157} This allows substantial extension of the range of AB block copolymers.

This can be done⁷³ by performing, *e.g.*, polymerisation of alkyl acrylates (including butyl acrylate) at elevated temperatures (428 K) in the presence of an iminoxyl radical, such as 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy.[†] This procedure was used for the synthesis of not only the AB diblock copolymers (A is poly(alkyl acrylate) and B is polystyrene), but also the ABA and BAB triblock copolymers, as well as the AA' diblock copolymers, where A and A' are alkyl acrylates differing in the type of the alkyl substituent.

The use of different types of polymerisation for the synthesis of blocks A and B was proposed.^{73, 158–160} In this case, stable iminoxyl radicals are modified by incorporation of additional functional groups with retention of the atomic group carrying the unpaired spin. 4-HO-TEMPO synthesised using the known procedure¹⁶¹ is the most appropriate for such a modification. In this case, the hydroxy group is modified. For instance, a poly(tetrahydrofuran-*b*-styrene) block copolymer was synthesised¹⁶² using a combination of cationic polymerisation to obtain poly(tetrahydrofuran) followed by 'living' radical polymerisation of styrene. First, 4-HO-TEMPO was treated with sodium hydride at room temperature to give 4-NaO-TEMPO which reacts with 'living' chains grown in the cationic polymerisation of tetrahydrofuran.



Being 'dead' in cationic polymerisation, poly(tetrahydrofuran) chains capped with the iminoxyl end group (block A) 'revive' in the bulk of styrene (or styrene derivatives and their mixtures with other monomers) and help the chain extension of the block B following the 'living' radical polymerisation mechanism. For instance, synthesis of the block B was performed in the presence of dibenzoyl peroxide (with alkoxyamine synthesised *in situ*) at 368 K over a period of 3.5 h and followed by heating at 398 K for 64 h.¹⁶² The molecular masses, polydispersities as well as the lengths of blocks A and B expressed in the numbers of THF

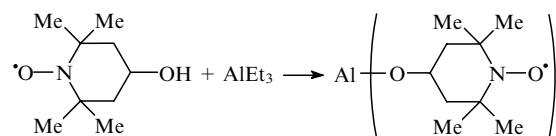
[†] Here,⁷³ the corresponding alkoxyamine was synthesised using azobis(isobutyronitrile) instead of dibenzoyl peroxide and polymerisation was performed at 378 K rather than at a conventional temperature of 363–368 K.

(block A) and styrene units (block B) for three specimens of the AB block copolymers were as follows:

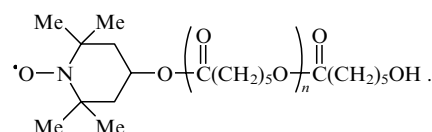
Parameter	Specimen 1	Specimen 2	Specimen 3
Block A			
M_n	1520	3300	10 600
M_w/M_n	1.38	1.43	1.26
n (THF)	14	24	77
Block B			
M_n	9690	12 600	38 800
M_w/M_n	1.22	1.25	1.40
n ($\text{CH}_2 = \text{CHPh}$)	103	112	337

The use of anionic polymerisation in conjunction with 'living' radical polymerisation for the synthesis of a block copolymer based on ϵ -caprolactone and styrene has been reported.¹⁶³

First, anionic polymerisation of ϵ -caprolactone was performed at room temperature in toluene solution for 3 h using tris(2,2,6,6-tetramethyl-1-piperidinyloxy-4-oxy)aluminium as catalyst.

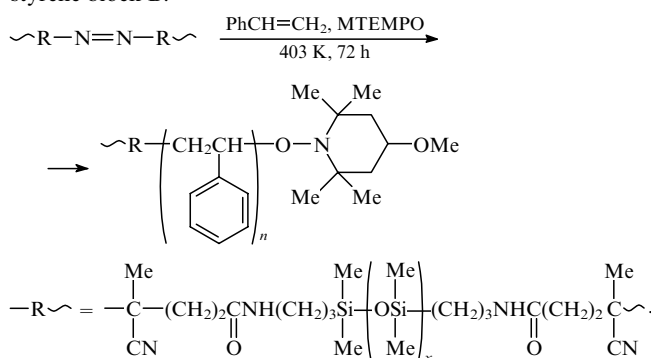


According to NMR data, this stage resulted in the formation of poly(ϵ -caprolactone) (block A) capped with the iminoxyl end group:



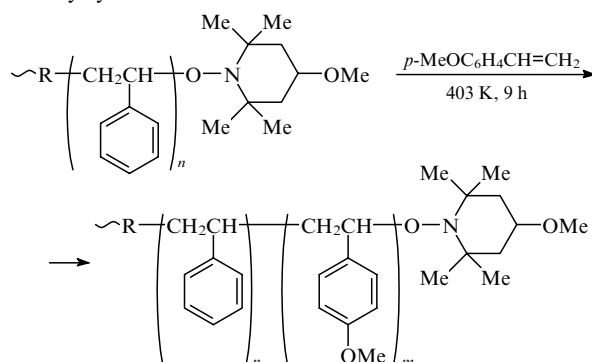
After isolation and purification, this block A was placed in the bulk of styrene, the iminoxyl group was *in situ* converted into the alkoxyamino group in the presence of dibenzoyl peroxide and a 'living' radical polymerisation of styrene (block B) was performed. The molecular masses and polydispersities varied respectively in the range $3200 \leq M_n \leq 6700$ and $1.28 \leq M_w/M_n \leq 1.33$ for blocks A and $20\,000 \leq M_n \leq 26\,200$ and $1.37 \leq M_w/M_n \leq 1.42$ for blocks B.

Yet another example of a combination of 'living' polymerisation performed in the presence of alkoxyamines with other types of polymerisation in order to prepare block copolymers has been reported.¹⁶⁰ Block A was prepared from poly(dimethylsiloxane) ($M_n = 5000$) telomerised with propylamine in the presence of 4,4'-azobis(4-cyanopentanoyl) dichloride. The macroinitiator (block A) thus formed was used for the initiation of 'living' polymerisation of styrene in the presence of 4-methoxy-2,2,4,4-tetramethyl-1-piperidinyloxy¹⁶⁴ (MTEMPO) to grow the polystyrene block B.



The degree of styrene conversion was varied between 70% and 85%. The 'living' AB block copolymer prepared in this manner

was used for chain extension of the next block B' built of *p*-methoxystyrene units.



After 9 h, conversion of *p*-methoxystyrene reached 96%, which indicated that it is much more reactive than styrene during 'living' radical polymerisation.

According to NMR data, the ratio of dimethylsiloxane (block A), styrene (block B) and *p*-methoxystyrene (block B') units in the ABB' block copolymer was 1 : 6.67 : 44.5. The molecular masses and polydispersities of the macroinitiator, AB and ABB' copolymers were as follows (GPC data):

Product	M_n	M_w/M_n
Block A (macroinitiator)	33 000	2.39
Copolymer AB	66 000	1.90
Copolymer ABB'	135 000	1.43

In addition to poly(dimethylsiloxane), poly(isobutylene),¹⁶⁵ poly(ethylene glycol),¹⁶⁶ polyethers,¹⁶⁷ polycarbonate¹⁶⁸ and polyamide¹⁶⁹ were also used as macroinitiators. There is a review dedicated to the synthesis of block copolymers by 'living' polymerisation using alkoxyamines.¹⁷⁰

Summing up, studies on the use of alkoxyamines for the synthesis of unusual block and graft copolymers (including grafting onto fullerenes) should be mentioned^{54, 70, 71, 151, 171–194} as well as those dedicated to the preparation of star-like and dendritic structures.^{54, 151, 171, 175, 187, 190–192, 195, 196}

8. Prospects for the use of alkoxyamines and related compounds

Very recently (in the year 1999), it became possible to alleviate many problems in the use of alkoxyamines as agents for 'living' polymerisation. It was shown^{52, 137, 185, 197–199} that the dissociation rate of the C–ON bond in alkoxyamines can be increased not only by introducing a phenyl substituent at the C atom of the monomer, but also by varying the nature of substituents at the nitrogen atom.

It was found that the use of di-*tert*-butylnitroxyl instead of traditionally used nitroxides, TEMPO or its derivatives, leads to weakening of the bond subject to dissociation in the alkoxyamine molecule to the extent that the rate constant for dissociation, k_1 , appears to be high enough for performing a 'living' polymerisation of monomers devoid of aromatic rings at 393 K. For *tert*-butyl acrylate, the rate constant k_1 equals 10^{-3} s^{-1} at 393 K. Polymerisation of *tert*-butyl acrylate in the presence of di-*tert*-butylnitroxyl and cumyl peroxide (with alkoxyamine synthesised *in situ*) was performed at 393 K. The 'living' type of the process was confirmed by both the increase in M_n with conversion and by the narrowing of MMD.

These examples indicate that the possibilities of the use of alkoxyamines in 'living' polymerisation can be extended.

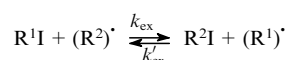
Obviously, other adducts RX which can decompose during polymerisation into two free radicals, *viz.*, an active radical R', which can react with the monomer M ($R' + M \rightarrow RM'$), and a stable radical X', which only can recombine with R' ($R' + X' \rightarrow RX$), can also act like alkoxyamines. Some of these compounds (*e.g.*, dithiocarbamates^{40, 41, 200}) were used well before

alkoxyamines. Currently, they are used much more rarely than alkoxyamines, most likely because of a larger number of side reactions which make 'living' polymerisation difficult. However, these and related compounds collectively called iniferters also have a number of advantages, the most important of which is photoactivity upon homolytic cleavage under the action of photoirradiation.

The search for new agents for 'living' radical polymerisation capable of undergoing a reversible photodissociation is one promising investigation line which seems to provide the possibility of substantial reduction of the operating temperature of the process (in the limit, down to room temperature). Low-temperature 'living' radical polymerisation of methyl methacrylate in the presence of RX containing piperidinothiocarbonylthio groups by photodissociation of the adduct RX instead of its thermal decomposition was attempted.²⁰¹

At present, intensive search for compounds capable of undergoing reversible homolytic cleavage in polymerisation systems is being carried out. 'Living' copolymerisation of styrene with methyl acrylate at 393 K in the presence of di(isopropoxythiocarbonyl) disulfide as RX was reported in 1997.²⁰² The polydispersity of the copolymer obtained in this manner was lower than that of its analogue synthesised by conventional radical polymerisation. (A linear increase in M_n with conversion was also observed in this study.)

Very recently, halogen-containing organic compounds have been evaluated for use as agents for 'living' polymerisation. 'Living'-chain radical polymerisation of styrene at 353 K in the presence of ω -polystyryl iodide as a mediator and dibenzoyl peroxide as an initiator has been reported.²⁰³ It was found that activation of the 'dormant' chains, RI, follows a radical substitution mechanism with the rate constant $k_{ex} = 3.1 \times 10^7 \exp(-27.8/RT) \text{ litre mol}^{-1} \text{ s}^{-1}$



rather than a reversible dissociation mechanism, $RI \rightleftharpoons R^\bullet + I^\bullet$. As can be seen, the activation energy of radical substitution reaction (27.8 kJ mol^{-1}) is much lower than that of thermal dissociation of alkoxyamines (124 kJ mol^{-1}).

Thus, the approach described above and based on the use of reversible homolytic cleavage of adducts RX remains rather promising. This is indicated by both an incessant stream of communications and the appearance of studies in which technological aspects are touched on.^{81, 204–211} To mention just a few: studies dedicated to the search for procedures for performing not only bulk polymerisation, but also polymerisation in aqueous solutions, as well as emulsion and dispersion polymerisation.^{81, 204–206, 210}

VI. Transition-metal halide complexes with organic ligands as agents for 'living'-chain radical polymerisation

Currently, an alternative approach to 'living' radical polymerisation is also being developed. This approach uses transition-metal compounds with mixed ligands including halogen atoms and organic ligands as agents for polymerisation. For brevity, we will call them transition-metal halides (TMH). The most commonly used compounds are transition-metal chlorides or bromides with the general formula $M^nY_nL_m$, where M is the transition metal, n is the valence of the transition metal, Y are the Cl^- or Br^- anions and L are organic ligands (as a rule, strong donors such as cyclic amines, linear polyamines, triphenylphosphine, *etc.*). The progress in this field is mainly associated with the studies by Matyjaszewski (USA).

Rapid development of the investigations on 'living' radical polymerisation controlled by the $M^nY_nL_m$ complexes is due to the fact that the new agents have three advantages over stable free radicals discussed in the previous Sections.

1. The most important is that, unlike TEMPO, the action of compounds $M^nY_nL_m$ is not confined to styrene and its derivatives, butyl acrylate, *etc.* as the monomers. On the contrary, these compounds can be used with almost all known monomers.

2. Compounds $M^nY_nL_m$ act at much lower temperatures (333–363 K)^{212, 213} than the TEMPO-type agents (393–428 K). It should be noted that the decrease in the operating temperatures makes it possible not only to solve the technologically important problem of reduction of power consumption, but also to reduce the risk of side reactions.

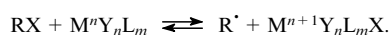
3. Using agents of the $M^nY_nL_m$ type, one can synthesise polymers with much narrower MMD and lower polydispersities ($M_w/M_n = 1.04–1.05$) than those of the polymers obtained with the TEMPO-type agents where $M_w/M_n \geq 1.15$ and often exceeds a value of 1.20.

Yet another (the most technologically important) advantage of compounds $M^nY_nL_m$ is that 'living' radical polymerisation can easily be carried out in friendly and environmentally safe aqueous solutions. Recently, the first studies on 'living' radical polymerisation in emulsions and dispersions in aqueous solutions have been reported.^{214, 215}

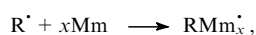
'Living' radical polymerisation controlled by agents of the $M^nY_nL_m$ type was called the Atom Transfer Radical Polymerisation (ATRP).

1. The mechanism of action

The mechanism of the action of $M^nY_nL_m$ compounds as agents for 'living' radical polymerisation is based on the known Kharasch reaction.²¹⁶ It was found that halides of transition metals in the lowest oxidation state n can react with alkyl halides RX to give alkyl radicals $R^\bullet$. This is accompanied by oxidation of the transition-metal atom. An essential feature of this reaction is its reversibility.



Obviously, performing the reaction in the bulk of a monomer (we will denote it Mm) initiates polymerisation by the mechanism $R^\bullet + Mm \rightarrow (R^1)^\bullet$, where $(R^1)^\bullet$ is the primary growing polymer chain, followed by incremental propagation of the primary chain by the reaction



where x is the number of the monomer molecules which to add to $R^\bullet$ during the time interval between the instant of appearance of the active polymerisation centre (as a result of the reaction between alkyl halide and $M^nY_nL_m$) and the instant of deactivation of this centre as a result of the reverse reaction with $XM^{n+1}Y_nL_mX$. Since activation occurs at regular time intervals, the deactivation is temporary, so that alkyl halide-induced polymerisation in the presence of $M^nY_nL_m$ is in essence implemented as a 'living'-chain process.

What actually happens is that the activation $\rightleftharpoons$ deactivation cycle proceeds in a more complicated manner rather than follows a simplified scheme discussed above. The reverse reaction involves a stage of addition of the free radical $R^\bullet$ to $M^{n+1}Y_nL_mX$ with the formation of an intermediate $R-M^{n+1}Y_nL_mX$, which is a mediator of stepwise growth of the polymer chain. Chain propagation occurs as the monomer addition to the radical $R^\bullet$ formed upon reversible decomposition of the intermediate rather than monomer insertion into the $R-M^{n+1}$ bond. The intermediate undergoes deactivation by decomposing into the alkyl halide RX and the initial complex $M^nY_nL_m$.

To initiate a 'living' radical polymerisation, one has to start either a forward or a reverse reaction of the activation $\rightleftharpoons$ deactivation cycle. When alkyl halides and $M^nY_nL_m$ are used as initiators, the forward reaction proceeds to give the active intermediate, $R-M^{n+1}Y_nL_mX$, which decomposes into the growing radical $R^\bullet$ and a complex $M^{n+1}Y_nL_mX$. If a halide of the transition metal in the highest oxidation state $[M^{(n+1)}]^\bullet$ is used, the active intermediate should be obtained in the reaction of

the complex $M^{n+1}Y_nL_mX$ with the radicals formed in the decomposition of the initiator [*e.g.*, azobis(isobutyronitrile)]. In both cases, 'living' radical polymerisation proceeds in the presence of the monomer. The most commonly used initiators are alkyl halides RX and complexes $M^nY_nL_m$;^{4, 212–214, 217–257} however, polymerisation can also be initiated by azobis(isobutyronitrile) in the presence of $M^{n+1}Y_nL_mX$ complexes.^{224, 227, 237, 258}

It should be noted that the process of 'living' radical polymerisation is often described using the concepts of a 'living' radical chain and a 'dormant' chain. If polymerisation is performed in the presence of stable nitroxyl radicals (TEMPO), a 'living' radical chain and a 'dormant' radical chain respectively mean a propagating radical $R^\bullet$ and an adduct (alkoxyamine TEMPO-R). For a polymerisation process proceeding in the presence of TMH, a 'living' radical chain also means a propagating radical $R^\bullet$ while a 'dormant' chain means an alkyl halide RX in the presence of $M^nY_nL_m$, where RX is either the initial alkyl halide or a polymeric product with the halogen atom in the end group. Polymer chains immobilised in the form of intermediates $R-M^{n+1}Y_nL_mX$ can be ignored since their concentrations are much lower than that of RX.

Thus, in both cases 'living' radical polymerisation is performed under conditions of dynamic equilibrium between the 'living' and 'dormant' radical chains.

The term 'living' chain, as applied to radical polymerisation, can also be used in another sense, much as in the case of, *e.g.*, anionic polymerisation. All chains which can grow are considered 'living'. These are all chains RX with the end group X which, under given conditions, can undergo homolytic cleavage to release an active free radical $R^\bullet$ (a growing polymer chain). In this case, it is believed that 'living' chains can be either 'dormant' in the form of RX or active in the form of $R^\bullet$.

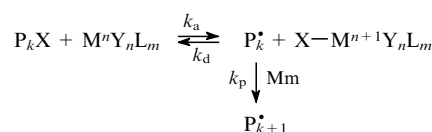
An essential distinction between TEMPO- and TMH-based agents for 'living' radical polymerisation is that the latter are catalytic systems and, unlike the former, are not incorporated into the polymer chains after completion of the polymerisation process. TMH-based agents can be separated from the polymer and re-used. However, this type of compound has a drawback consisting in the ability to initiate redox processes of polymer destruction.

The necessity of using well-defined terms can be illustrated taking calculations of the average lengths of polymer chains from the data on the degree of polymerisation, $\bar{P}$, as an example. As is known, $\bar{P} = \Delta[Mm]/[Mm]_0$, where $\Delta[Mm]$ is the concentration of polymer and $[Mm]_0$ is the initial monomer concentration. In this case, the chain length ν is defined by the ratio $\nu = \bar{P}[Mm]_0/[C]$, where $[C]$ is the concentration of chains. This implies that the $[C]$ value refers to all polymer chains grown in a given polymerisation system during the time interval $\Delta\tau$ needed to reach the specified $\bar{P}$ value. In other words, $[C]$ is the sum of the $[RX]$ value averaged over $\Delta\tau$ with averaged $[R^\bullet]$ value. If quadratic chain termination during time interval $\Delta\tau$ can be ignored, then, taking into account that $[R^\bullet]$ is negligible as compared to $[RX]$, it is admissible that $[C] \simeq [RX]_0 \simeq \text{const}$. Following this reasoning, all chains with the end group X are considered 'living'. The majority of calculations of ν rest on this consideration.

2. 'Living' radical polymerisation controlled by transition-metal halides

The simplest scheme of a 'living' radical polymerisation controlled by TMH is presented below (Scheme 6).^{259, 260}

Scheme 6



Here $P_k^\bullet$ is the growing polymer chain, X is a halogen, and k_a , k_d and k_p are the rate constants for chain activation, deactivation and propagation, respectively.

For $10^{-3} \text{ s} < t < 10^2 \text{ h}$, theoretical analyses^{88, 261} of Scheme 6 have led to a number of analytical expressions which

describe the kinetics of (i) polymerisation, (ii) reduction of instantaneous concentration of growing chains and (iii) increase in the instantaneous concentration of growing chain acceptor (a complex of the transition metal in the highest oxidation state, $X-M^{n+1}Y_nL_m$) throughout the process. The corresponding formulae are as follows:

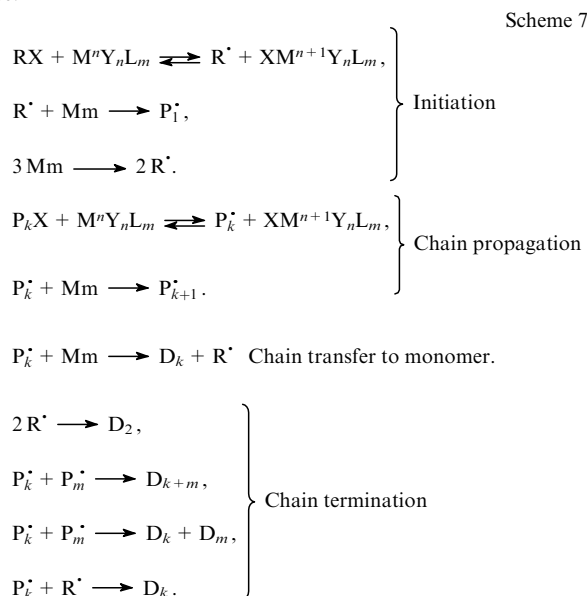
$$\ln \frac{[Mm]_0}{[Mm]} = \frac{3}{2} k_p ([RX]_0 [M^n]_0)^{1/3} \left(\frac{k_a t^2}{3k_d 2k_t} \right)^{1/3}, \quad (27)$$

$$[P_k^*] = ([RX]_0 [M^n]_0)^{1/3} \left(\frac{k_a}{3k_d 2k_t} \right)^{1/3}, \quad (28)$$

$$[M^{n+1}] = ([RX]_0 [M^n]_0)^{2/3} \left(\frac{3k_a^2 2k_t}{k_d^2} \right)^{1/3}. \quad (29)$$

Comparison of the results obtained after solving the system of differential equations (27)–(29) with the experimental results²⁵⁸ revealed considerable quantitative and qualitative (the shape of the kinetic curves) discrepancies between them.

To establish the reasons for such a sharp distinction between theory and experiment, computer simulation of a more detailed Scheme 7 was performed²⁵⁹ for Mm = styrene and M = Cu using the PREDICI programme package²⁶² and the results of reported studies.^{106, 262–266}



The numerical values of rate constants k used in computer simulation of a styrene polymerisation at 383 K with $[Mm]_0^*$, $[RX]_0^*$, $[M^n]_0^*$ and $[M^{n+1}]_0$ equal to 8.7, 0.087, 0.087 and 0 mol litre^{−1}, respectively, are shown below:

k /litre mol ^{−1} s ^{−1}	Numerical value	Ref.
k_i	1.6×10^4	267, 268
k_p	1.6×10^3	102
$2k_{tc}(0)$	10^9	267
$2k_{td}(0)^*$	10^8	267
$2k_{to}$	10^9	267
k_{tr}	0.22	269
k_d^*	1.1×10^7	270
k_a	0.45	270
k_{tp}	10^9	267, 271
k_{term}^*	4.8×10^{-11}	112

(the asterisked parameters were used as independent variables).

The discrepancies between the results of computer simulation and the known experimental data²⁵⁸ appeared to be as substantial as in the case of comparing with the results of analytical solutions of Eqns (27)–(29). Variation of the initial k values over a wide

range under assumption that they remain unchanged during the process does not make the situation better. It was found that calculated data can fit experimental results only assuming that the numerical values of particular rate constants vary during the process, *i.e.*, that they are dependent on the degree of conversion Γ (degree of polymerisation).

The appearance of the $k = f(\Gamma)$ dependence during polymerisation is largely caused by an increase in the viscosity of the reaction mixture. This prevents the reagent molecules A and B from approaching each other in the bimolecular reaction $A + B$ to the extent that the reaction becomes diffusion-controlled.^{267, 268, 272–290} In other words, after the viscosity of the reaction medium reaches a particular threshold (because of accumulation of the polymer), the rate of the bimolecular reaction $A + B$ appears to be controlled by the diffusion characteristics of A and B rather than their reactivities. Quantitatively, a bimolecular reaction goes under diffusion control if the condition $k > k_D$ (k_D is the rate constant for pairwise collisions between molecules A and B) is met. Evaluation of k_D according to Smoluchowski^{272, 277–283, 291}

$$k_D = 4\pi R(D_A + D_B)$$

(R is the distance between the centres of gravity of the colliding molecules and D_A and D_B are the diffusion coefficients of molecules A and B in the reaction medium) shows that for low-molecular mass compounds ($D \approx 10^{-5}$ cm² s^{−1}) the k_D value is $\sim 4 \times 10^9$ litre mol^{−1} s^{−1} for $\Gamma \approx 0$. This implies the absence of diffusion control over every elementary act (all k values are much less than 4×10^9). For dilute polymer solutions ($0 < \Gamma < 10\%$), the D value ($D \approx 10^{-7}$ cm² s^{−1}) is about two orders of magnitude smaller than for low-molecular mass compounds. Here, the threshold k_D value decreases down to $\sim 4 \times 10^7$ litre mol^{−1} s^{−1}, which is comparable with the rate constant for quadratic chain termination. For $\Gamma > 10\%$, polymer solutions become so viscous that the diffusion coefficients do not exceed 10^{-9} cm² s^{−1} and $k_D \leq 4 \times 10^5$ litre mol^{−1} s^{−1} even for low-molecular mass compounds. Thus, not only quadratic termination reactions of growing chains, but also elementary bimolecular reactions between small molecules (provided that their rate constants meet the condition $k \geq 4 \times 10^5$ litre mol^{−1} s^{−1}) go under diffusion control at $\Gamma > 10\%$.

The $k = f(\Gamma)$ dependence for high rate constants for quadratic chain termination, due to diffusion control of the corresponding elementary reactions, was also suggested.²⁵⁹ The corresponding formula is as follows^{292, 293}

$$k_T = k_0 \left(\frac{\Gamma [Mm]_0}{[RX]_0} \right)^{-(0.65+0.02 \frac{\Gamma [Mm]_0}{[RX]_0})},$$

where k_T is the current k value at a given degree of polymerisation Γ , expressed as the $[Mm]/[Mm]_0$ ratio ($\Gamma = \Delta[Mm]/[Mm]_0$), and k_0 is the k value at $\Gamma = 0$. Calculations performed using this model gave reasonable agreement with the experimental data.

Taking into account the known data on the diffusion kinetics,^{267, 268, 271–290, 292–294} the necessity of considering the diffusion-controlled character of quadratic chain termination reactions seems to be quite natural. Rather it is unclear why the neglect of this factor in the description of the mechanism of ‘living’ radical polymerisation in the presence of alkoxyamines causes no discrepancies between the calculated and the experimental data.

Clearly, there is no basic distinctions between the mechanism of the action of alkoxyamines and TMH (*cf.* Schemes 7 and 5). In both cases, pseudo-‘living’ chains (growing free radicals) are formed. At regular intervals, they are ‘revived’ and can react both with the monomer and with one another (unlike true ‘living’ chains which never react with one another).

It seems likely that the main distinction between TMH and alkoxyamines as agents for ‘living’ polymerisation has a purely quantitative character and lies in the fact that for TMH the rate constants for activation of ‘dormant’ chains are two orders of

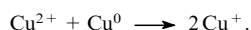
magnitude higher than the corresponding rate constants for alkoxyamines. Because of this, the repetition frequency of the dissociation $\rightleftharpoons$ recombination cycle responsible for the initiation of 'living' radical polymerisation increases substantially in the presence of TMH (see Scheme 7). This leads to a decrease in the 'sensitivity' of the polymerisation process to additional initiation (e.g., thermal initiation in the case of styrene) and to reduction of the polydispersity ($M_w/M_n \approx 1$). Probably, the increase in the 'sensitivity' of the process to the dependence of the rate constants for quadratic chain termination reactions on the degree of conversion is also due to an increase in the repetition frequency of the cycle, which necessarily requires consideration of the diffusion control of the rates of these reactions.

Detailed studies of the mechanism of ATRP showed first of all that, generally, the reaction follows a radical mechanism. It was found that introduction of strong inhibitors (galvinoxyl) results in complete suppression of polymerisation, whereas the additives of poisons of anionic and cationic polymerisation (alcohols and water) have no effect on the process.^{213,295} This undoubtedly confirms that ATRP follows the radical mechanism.

The question may also arise as to whether the polymer chain propagation occurs in this case by insertion of the monomer molecule into the $R-M^{n+1}Y_nL_mX$ bond (a conventional mechanism involves homolysis of the $R-M^{n+1}$ bond followed by the reaction of the released free radical with the monomer). Obviously, it is impossible to answer this question experimentally; however, most of investigators believe that chain propagation occurs in a normal manner rather than involving the monomer insertion.^{213,231,296}

It should also be noted that, according to Scheme 7, the reaction of chain termination should result in a polymer with halogen atoms as the end groups. This was observed experimentally.^{295,297} In addition, it was shown that polymerisation of a fresh portion of the monomer can be initiated by introducing the polymers with Cl or Br atoms as the end groups (of course, in the presence of catalytic amounts of $M^nY_nL_m$).²⁹⁵

An interesting study aimed at elucidating the mechanism of ATRP was carried out by Matyjaszewski and co-workers²⁹⁸ who investigated a catalytic system based on $CuBrL_m$. The addition of finely dispersed copper to the components of the system resulted in the transformation of $CuBr_2$ formed in the course of the reaction into active $CuBr$ which rapidly reacted with RX (RBr).



This redox reaction promoted a substantial increase in the initiation rate. As a result, the rate of polymerisation increased by more than an order of magnitude and complete conversion was reached after 55 min. The redox reaction between Cu^{2+} and Cu^0 was confirmed by ESR spectroscopy. There is no question that this approach and related investigations into the processes of activation of 'living' radical polymerisation are also technologically important.

3. Catalytic systems based on transition-metal halides and the assortment of polymeric products formed

Studies on 'living' polymerisation using TMH are primarily dedicated to the search for the most efficient catalytic systems using semiquantitative evaluation procedures. It was found that the most efficient systems are based on copper bromide.^{212,219,231} It is these catalytic systems that allowed the synthesis of polymers with $M_w/M_n = 1.04-1.05$ and molecular masses $M_n = (50-100) \times 10^3$. This has initiated intensive search for novel catalytic systems without accompanying detailed kinetic studies. However, systems based on other transition metals appeared to be less efficient as regards both the polydispersity index, M_w/M_n , and the molecular mass M_n . Currently, catalytic systems containing chlorides and bromides of $Cu(I)$ and $Cu(II)$,^{4,212-214,217-249,299,300} $Fe(II)$,^{250,301-303} $Ni(II)$,³⁰⁴⁻³¹⁰

$Ru(II)$,^{215,295,296,311-320} $Rh(II)$,^{221,321} acetates of $Pd(II)$ ³²² and $Cr(II)$,³²³ as well as ReO_2 (see Ref. 324) have been studied (Table 3). For all the salts, except for $CuBr$ and $CuCl$, the polydispersity indices, M_w/M_n , lie between 1.1 and 1.3.

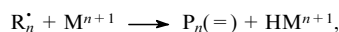
Syntheses of polymers with $M_w/M_n = 1.04-1.05$ have clearly demonstrated that quadratic chain termination contributes insignificantly to the MMD of the polymers. A semiquantitative procedure developed for the analysis of experimental results is based on the determination of the dependences of $\ln([Mm]_0/[Mm]_t)$ on t , where $[Mm]_0$ and $[Mm]_t$ are the initial and running concentrations of the monomer, respectively. The results of testing were accepted if both dependences were linear.

This procedure was used to analyse a large number of catalytic systems. For instance, organic ligands (L) were varied in studies of the catalysts based on $CuBr$. If both the above-mentioned dependences were linear, the effect of the nature of the ligand on the polydispersity index was followed and those ligands were chosen which gave polymers with the smallest M_w/M_n ratios. The effect of ligands on the solubility of TMH in the monomers (solvents) was also taken into account^{212,213,231} and then the ligands which were the best to stabilise the ions of metals in the highest oxidation state were chosen from the group of preliminarily selected compounds. This made it possible to choose the systems with the highest concentrations of active intermediate $R-M^{n+1}Y_nL_mX$. As follows from the data listed in Table 3, bipyridines and polyamines appeared to be the best ligands, whereas triphenylphosphine appeared to be the worst one. This is likely due to the fact that triphenylphosphine *per se* can be involved in the redox cycle.

Apparently, ligands can also suppress a number of possible side reactions such as (presumably) oxidative chain termination (for simplicity, the ligands at TMH are not shown):



and (or) hydride transfer:



where $P_n(=)$ is the polymer with the end group containing a double bond. Such radical reactions are known for transition-metal salts and complexes.³²⁵ Both reactions result in chain termination and, hence, in broadening of MMD and an increase in M_w/M_n . (Scheme 7 discussed in the previous subsection ignores these reactions since it corresponds to the case $M = Cu$ where the neglect of these side processes is well substantiated.)

A similar procedure was used for studying and choosing alkyl halides (RX). In this case, the results of bulk polymerisations and polymerisations in solvents were compared. The M_w/M_n ratio was analysed as a function of the degree of conversion.

Almost all catalysts listed in Table 3 make it possible to obtain better values of M_n and M_w/M_n than TEMPO. In addition, these catalytic systems allow polymerisation of almost all vinyl monomers at lower temperatures.

In addition to catalytic systems, activators have also been studied. Aryl and sulfonyl halides were found to be the best activators of 'living' polymerisation, alkyl halides are less efficient. In the latter case, the role of activator is played by the second component of the binary system, which 'works in pair' with the catalyst ($M^nY_nL_m$ or $M^{n+1}Y_nL_mX$). For compounds $M^nY_nL_m$, alkyl halide RX acts as activator (the initial pair is $RX + M^n$), whereas for compounds $M^{n+1}Y_nL_mX$ this role is played by the source of free radicals, such as azodinitrile, *etc.* (the initial pair is $R^* + M^{n+1}$).

It is believed^{212,213,231} that the rate of the redox reaction between the activator and catalyst should be high enough to provide nearly simultaneous initiation of all chains; this is one of the main conditions for the preparation of polymers with narrow MMD and very low polydispersity M_w/M_n . The choice of compounds to be used as activators is performed to meet this condition.

Table 3. Catalytic systems for ATRP based on transition-metal compounds.

Metal compound and its concentration/mol litre ⁻¹	Ligands (L) and their concentrations/mol litre ⁻¹	Activator (A) and its concentration/mol litre ⁻¹	<i>T</i> /K	<i>t</i> /h	Main characteristics of polymer				Ref.
					type of the monomer (Mm) ^a	conversion (%)	<i>M_n</i>	<i>M_w/M_n</i>	
CuBr 3 × 10 ⁻²	4,4'-di(nonan-5-yl)-2,2'-bipyridine 6 × 10 ⁻²	diphenylethyl bromide 6 × 10 ⁻²	383	5	MA	95	17 000	1.05	219
					St	95	50 000	1.05	
CuBr 5.53 × 10 ⁻²	2,2'-bipyridine 5.53 × 10 ⁻²	2-bromopropionitrile 5.53 × 10 ⁻²	317	23	AN [solution in ethylene carbonate (5.25 mol litre ⁻¹)]	38.3	10 000	1.04–1.06	240
CuBr ₂ 4.5 × 10 ⁻²	4,4'-di(nonan-5-yl)-2,2'-bipyridine 9 × 10 ⁻²	azobis(isobutyronitrile) 4.5 × 10 ⁻²	383	16	St	90	50 000	1.15	224
			383	10	MA	90	9 000	1.1–1.15	
			383	8	MMA		16 000	1.2–1.4	
CuCl [Mm]:[CuCl]:[A]:[L] = 200:1:1:3	2,2'-bipyridine	MeSO ₂ Cl	363	5–6	MMA	89		1.35	225
			403	5–6	St	89		1.49	
			493	5–6	BMA	98		1.27	
CuBr 1.05 × 10 ⁻²	4,4'-di(nonan-5-yl)-2,2'-bipyridine 2.01 × 10 ⁻²	<i>p</i> -toluenesulfonyl chloride	363	5	MMA (solution in biphenyl ether)	85	184 000	1.5	236
[CuBr]:[Cu ⁰] = 1:10	4,4'-di(nonan-5-yl)-2,2'-bipyridine [A]:[CuBr]:[L] = 1:2:0.4	methyl 2-bromopropionate	363	0.9	St	96	50 000	1.1–1.3	298
CuCl [Mm]:[A]:[CuCl] = 200:1:2	4,4'-di(nonan-5-yl)-2,2'-bipyridine	4,4'-di(chlorosulfonyl)-biphenyl	413	2.5	BA		30 000	1.5	213
CuBr 9 × 10 ⁻²	1,1,4,7,10,10-hexamethyltriethylenetetraamine 4.7 × 10 ⁻²	1-phenylethyl bromide 9 × 10 ⁻²	363	8	MMA	90	20 000	1.1	224
			383	8	MA	80	20 000	1.2	
			383	8	St	80	20 000	1.15	
FeBr ₂ 10 ⁻²	4,4'-di(nonan-5-yl)-2,2'-bipyridine	1-phenylethyl bromide	353	15	MMA		75 000	1.24	303
			383	12	St	64	7 000	1.27	
FeCl ₂ 10 ⁻²	triphenylphosphine 0.1	CCl ₄ 10 ⁻²	353	60	MMA	90	2 000	1.3–1.4	302
RuCl ₂ 10 ⁻² (aluminium isopropoxide as a co-activator)	triphenylphosphine 0.1	PhCOCHCl ₂	353	81	MMA	97	10 000	1.3	296, 314
[NiCl ₂] = 10 ⁻² (aluminium isopropoxide as a co-activator)	triphenylphosphine	CCl ₃ Br 2 × 10 ⁻²	353	12	MMA [solution in benzene (2 mol litre ⁻¹)]	48	5 200	1.21	306
CuBr 0.1	4,4'-di(nonan-5-yl)-2,2'-bipyridine 2 × 10 ⁻²	benzyl bromide 0.1	363–373	—	MMA	95	10 000	1.2	217
ReO ₂ (aluminium isopropoxide as a co-activator)	triphenylphosphine	MeCH(Ph)I 6 × 10 ⁻²	373	8	St	94	40 000	1.15	324
ReO ₂ [ReO ₂ (PPh ₃) ₃] = 6 × 10 ⁻²	triphenylphosphine	—	353	25	St	98	9 900	1.4	324
			333	25	St	93	9 900	1.32	
			303	25	St	83	8 500	1.6	
Pd(OAc) ₂	triphenylphosphine [Pd(OAc) ₂]:[CCl ₄] = 10:1	CCl ₄	343	24	MMA	74	30 000	1.6	322
CuBr	2,2'-bipyridine	methyl 2-bromopropionate	363	15	2-hydroxyethyl acrylate	~100	6 270	1.2	
CuCl 10 ⁻²	<i>N,N',N'',N''',N''''</i> -pentamethyldiethylenetetramine 10 ⁻²	1-phenylethyl bromide 10 ⁻²	313	8	VP	85	15 500	1.17	230

^a Notations: MA is methyl acrylate, St is styrene, AN is acrylonitrile, MMA is methyl methacrylate, BMA is butyl methacrylate, BA is butyl acrylate and VP is vinylpyridine.

4. ‘Living’ radical polymerisation performed in emulsions, suspensions and with the use of immobilised catalysts

As was mentioned above, intensive studies on ‘living’ radical polymerisation have led to the discovery of relatively simple and cheap catalytic systems which make it possible to accomplish the

polymerisation process in several hours and to obtain well-defined polymers with molecular masses as high as 10⁵ monomer units and narrow MMD (*M_w/M_n* ≈ 1.05–1.1).

It is obvious that bulk polymerisation faces some problems associated with fast heat transfer from the reaction zone and with

an increase in the viscosity of the reaction media during the process. Additionally, catalysts should be removed from the polymer after completion of the process, since usually they have an intense colour and can oxidise polymers under operating conditions.

Polymerisation in solvents also has essential drawbacks such as fire hazard, necessity of solvent regeneration and environmental costs.

Suspension or emulsion polymerisation in water-borne systems seems to be best suited to overcoming all the above-mentioned problems.

However, no studies on the emulsion^{214, 326} and suspension²¹⁵ 'living' radical polymerisation had been reported until 1999. The results obtained recently are encouraging, since emulsion polymerisation is at least as efficient as bulk polymerisation.

Matyjaszewski *et al.*²¹⁴ found that emulsion polymerisation of butyl methacrylate using CuBr_2L as catalysts allows reduction of the temperature of the process from 363 to 343 K and shortening of the polymerisation time from 20 to 4–5 h. The monomer conversion reached $\sim 90\%$, as is the case of bulk polymerisation. However, it should be noted that MMD was somewhat broader and varied between 1.1 and 1.2 instead of being equal to 1.05.

The new approach has of course posed some problems associated with the choice of initiators and emulsifying agents, buffer solutions, *etc.*, including the problem of stability of the latex species against aggregation as well as the problem of confining the catalysts to the monomer phase. Nevertheless, there is reason to believe that all these problems will be successfully solved since the mechanism of the action of catalysts in binary systems remains essentially the same.

'Living' radical polymerisation in suspensions have also been studied by investigators from Japan.²¹⁵ Polymerisation of MMA was performed at 353 K using $\text{RuCl}_2(\text{PPh}_3)_3$ as the catalyst. Monomer suspensions in a toluene–water mixture as well as in alcohols with additives of CH_2Cl_2 and water were used. Fairly good results were obtained, the polymers were characterised by $M_n \approx 10^5$ and $M_w/M_n = 1.1–1.3$. Stability of suspensions was achieved by vigorous stirring of the mixtures.

Finally, Matyjaszewski²¹³ attempted to immobilise CuBr_2L_2 -based catalytic systems using silica gel and cross-linked polystyrenes as catalyst's supports. However, polymerisations of styrene in the presence of immobilised catalysts were unsuccessful, namely, the M_w/M_n ratio varied in different experiments between 1.5 and 10 (for $M_n = 10^4–10^5$). The reasons why MMD is so broad are likely associated both with the diffusion from the matrix supporting the immobilised catalyst and with the increase in the molecular mass of 'living' chains during conversion. Despite the failure, the author intended to continue his studies since immobilisation of catalysts results in considerable reduction of contamination of the polymeric products by metal-containing impurities.

5. Synthesis of block, graft, star and hyperbranched copolymers using atom transfer radical polymerisation

It is well known that block copolymers, as well as star and other copolymers were first synthesised using a 'living' cationic and anionic polymerisation of vinyl monomers (their number is limited, however). Obviously, 'living' radical polymerisation would favour the extension of the assortment of different types of copolymers and, correspondingly, the broadening of the spectrum of their consumer properties.

A procedure for the preparation of block copolymers by 'living' chain polymerisation is simple. First, polymerisation of a monomer A is performed until complete conversion. Then, the other monomer (B) is introduced into the reaction system to yield a block copolymer AB. The blocks can alternate in any manner.

Star copolymers are synthesised using polyfunctional activators (alkyl halides, sulfonyl halides, *etc.*) with more than one active halogen atom. In the reaction with a catalyst (*e.g.*, $\text{Cu}^{\text{I}}\text{BrL}_2$), these halides are transformed into 'living' chains so that each polyfunctional (with respect to the halogen) molecule becomes the initial point for the growth of several polymer chains which form a star-

like structure. Synthesis of star copolymers with two, three, five^{213, 311} and even eight arms has been reported.²¹²

Graft copolymers are prepared using the reaction of chain transfer to polymer. In this case, the monomer simultaneously plays the role of an activator since halogen atoms are constituents of the monomer molecules. Almost all of them can be the initial points for chain propagation. A number of studies on the synthesis of this type of polymers has been reported.^{223, 327, 328}

It is known that both anionic and cationic polymerisation require extremely pure reagents and solvents with complete exclusion of water. 'Living' radical polymerisation allows nearly complete elimination of these limitations. Recently, numerous syntheses of almost all types of copolymers by 'living' radical polymerisation of a broad spectrum of monomers have been reported.^{229, 231, 235, 305, 306, 311, 329, 330} For instance, diblock and triblock copolymers of alkyl methacrylates,^{305, 331} styrene and acrylates,^{213, 312} polysulfones and styrene²²² and some other linear copolymers have been prepared.^{212, 213, 296, 314}

An interesting procedure for the synthesis of block and graft copolymers involves a combination of cationic polymerisation with ATRP.^{233, 246, 249, 332–334} In the first stage, cationic polymerisation of a monomer A is used to grow the chains with halogen-containing end groups (macromonomers), which are then involved in the ATRP process which proceeds in the bulk of a monomer B. This procedure was used for the preparation of various diblock copolymers of the AB type, where A is poly(tetrahydrofuran),²⁴⁶ ϵ -caprolactone,³³² vinyl ethers,²³³ norbornene or cyclopentadiene,²⁴⁹ as well as bicyclic alkenes such as bicyclo[2.2.1]heptene and bicyclo[2.2.1]heptadiene³³³ (cationic polymerisation), and B is polystyrene or poly(meth)acrylates (ATRP process).

VII. Three-dimensional 'living'-chain radical polymerisation

Polyfunctional unsaturated oligomers are compounds the molecules of which contain more than one double bond (glycol dimethacrylates, divinylbenzene, oligoester acrylates,^{335–338} oligoester maleates,³³⁹ *etc.*). Polymerisation of these compounds results in the formation of polymer networks (three-dimensional structures). Unlike linear polymerisation of conventional vinyl monomers, three-dimensional radical polymerisation proceeds according to a specific (the so-called microheterogeneous) mechanism^{336, 337} to give a specific type of topological and supramolecular (morphological) structure of the polymeric product. A salient feature of the topological structure of the polymer is that a large number of small rings is formed in the polymer network.^{144–146} These rings play the role of defects in the continuous network. A peculiarity of the morphology is that a 'grain' structure is formed in the polymer and the inter-'grain' spacings are considered as defects of the supramolecular structure.

The appearance and development of topological and morphological defects during three-dimensional radical polymerisation is due to the chain character of the polymerisation process.^{336, 337} That is, the chains initiated upon decomposition of the initiator rapidly (nearly instantaneously in the time scale of complete conversion) grow until the final length and undergo termination. The reaction system built of branched, cross-linked and aggregated polymer chains is thermodynamically and kinetically unstable in the bulk of the initial oligomer. Because of this, microphase separation occurs in the system, enhanced by a local gel effect. Eventually, this is the reason for the formation of defects, which affects physicomechanical characteristics of this type of polymer and materials based on them.

Since unsaturated oligomers have found wide and technologically important use,^{335–339} investigators are in continuous search for the ways of eliminating the reasons for the formation of defects during their polymerisation. In this regard, 'living' chains play a special role. Actually, transformation of a conventional three-dimensional chain polymerisation into 'living' chain polymer-

isation makes the process stepwise, which is typical of such well-known oligomers as epoxides, urethanes and polycondensation resins. A small distinction between 'living'-chain polymerisation and stepwise process is only that each initiation act causes the propagation of growing polymer chains by several monomer units rather than one unit. Thus, the increment value for stepwise 'living' radical polymerisation exceeds unity (one monomer unit), which makes it possible to call this process a pseudostepwise one. In this case, the reasons for intense formation of defects, inherent in three-dimensional radical polymerisation, are eliminated.^{336, 337}

Only a few studies on three-dimensional 'living'-chain radical polymerisation have been reported to date.^{72, 143, 340–343}

Ide and Fukuda^{72, 340} studied three-dimensional 'living' radical copolymerisation of styrene with 4,4'-divinylbiphenyl at 398 K in the presence of alkoxyamine synthesised from styrene and a TEMPO-like nitroxide. They determined the copolymerisation constants including that of styrene with 'pendent' double bonds of 4,4'-divinylbiphenyl, $r_p = k_{11}/k_{1p} = 1.0 \pm 0.1$ (the subscripts 'l' and 'p' correspond to styrene and divinyl oligomer, respectively). Since $r_1 = k_{11}/k_{12} = 0.38$, it was concluded that intense cyclisation on 'pendent' bonds, inherent in conventional radical chain polymerisation in this system, ceases nearly completely upon transformation of the process into 'living' polymerisation. It was also found that the end product, a cross-linked polystyrene (or a polystyrene network), was almost free from small-cycle topological defects.

A comparative study of the properties of polystyrenes cross-linked with 4,4'-divinylbiphenyl synthesised using conventional radical polymerisation (without TEMPO) and 'living' radical polymerisation (in the presence of TEMPO) has been reported.³⁴⁰ Specimens of identical composition prepared in the presence and in the absence of TEMPO possessed substantially different properties. These differences were interpreted in terms of the microheterogeneous model.³⁴⁰ The specimens synthesised by 'living'-chain polymerisation were identified as 'homogeneous'. They were characterised by nearly random distribution of cross-link points of the polymer network in the bulk of the copolymer. The specimens prepared in the absence of TEMPO were identified as 'microheterogeneous'. Their structure comprised a loose network built of highly cross-linked microgel aggregates. It was also found that, for the same concentration of cross-link points of the polymer network per unit volume, 'homogeneous' specimens had appreciably larger modulus of elasticity and greater swelling and, hence, longer fragments between the cross-link points of the polymer network (calculations by the Flory–Renner method) than 'microheterogeneous' specimens.

'Living' three-dimensional radical homopolymerisation and copolymerisation of diethyleneglycol dimethacrylate with different monomers and oligomers in the presence of *p*-xylylenebis(*N,N*-diethyl dithiocarbamate), which undergoes reversible dissociation upon photoirradiation ($\lambda = 365$ nm), has been studied.^{341–343} Temperature and frequency dependences of the modulus of elasticity and the loss factor $\tan \delta$, as well as the spectra of relaxation times and thermal characteristics of the homo- and copolymers were measured using dynamic mechanical analysis. Judging from the pattern of the distribution of relaxation times, it was concluded that microheterogeneity in the specimens increases as the density of the three-dimensional polymer network increases.

However, it is impossible to evaluate the extent to which the defectiveness of the specimens prepared by 'living' polymerisation decreases using the results obtained in these studies. An indirect confirmation of the efficiency of 'living'-chain polymerisation can be obtained from the results of ESR measurements of the concentrations of stabilised methacrylate radicals (chain carriers). According to ESR data, the concentration of chain carrier radicals in the specimens of highly cross-linked methacrylates is low, while specimens prepared by conventional radical polymerisation are characterised by high concentrations of methacrylate radicals. Moreover, these radicals do not recombine at room temperature over a long time (days and even months). Such a high stability of

methacrylate radicals is due to inhomogeneous distribution of the cross-link points of the polymer network in the bulk of the material and to the presence of microscopic domains with extremely dense polymer network in which stabilisation ('freezing') of chain carrier radicals occurs.^{336, 337, 344}

Three-dimensional radical copolymerisation of styrene with dimethacrylates in the presence of alkoxyamines was also studied.¹⁴³ It was established that the process under study was 'living'-chain polymerisation and specimens were synthesised for studying their microheterogeneities using the known procedure^{336, 337} and for measuring their physicochemical characteristics. It is believed that further comparison of these polymers with related materials obtained by conventional radical polymerisation will make it possible to solve the problem of the efficiency of three-dimensional 'living'-chain polymerisation of unsaturated oligomers.

VIII. Other agents for 'living' radical polymerisation

Most of the studies discussed in the previous Sections have been devoted to two (the main, in our opinion) investigation lines in the area of 'living' radical polymerisation. These are implementation of 'living'-chain polymerisation in the presence of (i) alkoxyamines (or stable nitroxyl radicals introduced into the polymerisation system in order to synthesise alkoxyamines *in situ*) and (ii) halide transition-metal complexes with organic ligands (or their components for the *in situ* synthesis). The choice of the investigation lines to be reviewed was dictated by two reasons, namely, the number of studies reported to date and, which is more important, the reliability of experimental results (all the data mentioned above were repeatedly reproduced by several independent research groups). This made it possible to give reliable formulations of the main kinetic features and the mechanism of the polymerisation processes under study. However, the list of studies carried out in these two investigation lines is far from being exhaustive. Below, we will outline some other lines of scientific exploration in the area of 'living' radical polymerisation.

Currently, studies of 'living' radical polymerisation have been carried out for a wide range of compounds capable of forming reversible adducts with labile bonds (e.g., C–S,^{345–348} C–Co,^{10, 349} C–Al^{350–352} and C–X (X = Cl, Br, I)^{313, 353–356} bonds) upon reactions with growing polymer chains.

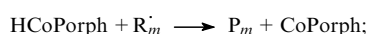
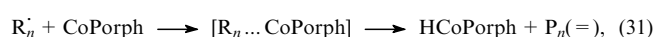
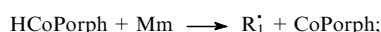
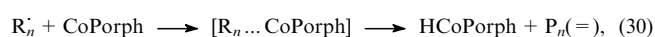
Compounds with the C–S and C–X bonds were called iniferters, since they simultaneously act as the chain *initiators*, *transfer* agents and *terminators*. Thermal and photo-iniferters are known; their studies began in the 1980s.³⁵⁷

In writing the review 'living' radical polymerisation in the presence of iniferters was deliberately excluded from consideration. The development of this investigation line is associated with the studies by Otsu (Japan) who seems to be the pioneer of this area. Our decision was due to the fact that a comprehensive review covering the problem was published in 1998.³⁵⁸ All classes of iniferters were considered which were found to be the most efficient agents for 'living' polymerisation. The review concerns mono-, di-, tetra- and polyfunctional iniferters which reversibly dissociate being exposed to light (photo-active agents) or on heating, as well as monomeric, polymeric or microdisperse (microgel) iniferters used for the synthesis of monofunctional, telechelic or polyfunctional polymers, block and graft copolymers, branched (dendritic), star and cross-linked polymers. Thermally active iniferters were considered taking phenylazotriphenylmethane and tetraphenylethane derivatives as examples. The group of photo-active iniferters was represented by organosulfur compounds. Mention was made that compounds with the *N,N*-diethyldithiocarbamoyl groups were found to be the most efficient.³⁵⁹

The use of macrocyclic cobalt compounds (MCCC) appeared to be quite efficient for performing a 'living' radical polymerisation of acrylic monomers. This procedure was used for the synthesis of, e.g., well-defined poly(methyl acrylates) with

$M_n \approx 50\,000$ and $M_w/M_n = 1.1$.³⁴⁹ It was found that the mechanism of the action of MCCC is essentially different from that of mixed-valence metal compounds (see Section VI) since cobalt is not involved in the redox reactions during reversible formation and decomposition of the labile adducts of MCCC with growing polymer chains.

Detailed study of porphyrin-based MCCC showed that the active intermediate R—CoPorph formed upon trapping by cobalt porphyrin complexes can decompose in different ways depending on the type of trapped radical and reaction conditions. Possible pathways of the decomposition are three catalytic reactions described in a monograph¹⁰ (see also Refs 6–9 and 11–33).



Here, CoPorph is a cobalt porphyrin (phthalocyanine, or gly-oxime) complex; R'_n , R'_m and R'_l are radicals with the degree of polymerisation equal to n , m and l , respectively; M_m is monomer, $P_n(=)$ is macromolecule with the double bond in the end group, $[R_n \dots \text{CoPorph}]$, $[R_{n+1} \dots \text{CoPorph}]$ are reactive intermediates with the C—Co bond and $[\text{HCoPorph}]$ is porphyrin cobalt hydride.

Reactions (30)–(32) were called catalytic chain transfer, catalytic inhibition and reversible inhibition reactions. The last-named reaction was observed in the polymerisation of acrylates; however, the process showed some but not all features of 'living' polymerisation, apparently because it was accompanied by side reactions (30) and (31). More recently,³⁴⁹ suppression of side reactions by introducing axial ligands into CoPorph was reported by researchers from the United States.

Porphyrins and related ligands seem to be of limited use in the polymerisation of acrylates only. At least, our studies showed that effective control of chain propagation can be achieved only in this case.

Vigorous catalytic chain transfer reactions were observed in the case of polymerisation of MMA and styrene. Using this reaction, one can obtain oligomers up to a dimer (at CoPorph concentrations of $\sim 10^{-2}$ mol litre⁻¹). At first glance, introduction of axial ligands into CoPorph could promote transformation of this reaction into reversible inhibition. However, polymerisation of both MMA and styrene in the presence of CoPorph with axial ligands (quinoline, pyridine, etc.) revealed the catalytic inhibition reaction. The nature of the radical seems to play the key role in the reactions with CoPorph and related compounds, so that only the nature of the polymer radical dictates which of reactions (30)–(32) will actually occur.

In conclusion, mention may be made that studies concerned with purely technological problems, except for a few references in the Sections concerning emulsion, suspension and solution polymerisation, have not been covered in this review.

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Mechanochemistry of catalysts

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Abstract. Data on the use of mechanochemical activation for the preparation of catalysts and supports are generalised. The effect of mechanochemical activation on the catalytic properties of various systems is noted. Catalytic reactions occurring under conditions of mechanochemical activation are discussed. The hypotheses concerning the nature of the effect of mechanochemical activation on the reactivity (including catalytic properties) are considered. The bibliography includes 197 references.

I. Introduction

An interesting, though, in our view, insufficiently studied problem is the application of mechanochemistry to heterogeneous catalysis. In both these fields, investigators are still on the way to creating general theories which would allow prediction of the behaviour of solids in various chemical and catalytic processes. In mechanochemistry as well as in catalysis, much is dependent on the solution of the problem of revealing catalytically active and reactive centres. For this reason, studies carried out at the borderline of the two sciences can favour to a considerable extent their mutual enrichment.

The development of mechanochemistry has begun with studies of grinding processes. It was found that grinding changes not only the sizes of particles of a material, but also their physicochemical properties. This provided the ground for introducing the term 'mechanochemical activation' (MCA). Grinding of substances is widely used in the chemical industry, including preparation of catalysts. The processes occurring under mechanical treatment of solids are described in sufficient detail in a number of monographs and reviews,^{1–5} and we will not dwell upon them. Let us only note the consequences of mechanochemical treatment on catalytic properties of solids or on the synthesis of catalytic systems.

Physicochemical changes resulting from MCA are the consequence of relaxation of the field of stresses in a solid after

mechanical impact on it. In all cases, irrespective of the relaxation mode, changes in the thermodynamic potentials of compounds under activation occur. The physicochemical properties of substances are related to the free energy G , for example,

$$\Delta G = -RT \ln \frac{k_2}{k_1},$$

$$\Delta G = RT \ln \frac{c}{c_\infty},$$

$$\Delta G = RT \ln \frac{p}{p_\infty},$$

$$\Delta G = \frac{-\lambda \Delta T}{T_p},$$

where k_1 and k_2 are the rate constants of forward and reverse reactions, c and c_∞ are the current and equilibrium solubilities, p and p_∞ are the current and equilibrium vapour pressures, λ and T_p are the heat and temperature of a phase transition, respectively. The free energy in turn depends on the sizes of particles of a compound and the presence of defects in it.

$$\Delta G = 2\sigma V \left(\frac{1}{r_1} - \frac{1}{r_2} \right),$$

where σ is the surface tension, V is the molar volume, r_1 and r_2 are the radii of the particles of fine and coarse fractions, respectively;

$$\Delta G = -kT \ln W,$$

where k is the Boltzmann constant, W is the thermodynamic probability equal to the possible modes of the distribution of defects in the lattice. It should be noted that the symbols r_1 and r_2 refer not only to the real physical size of particles but also to the sizes of ordered areas between the extended defects.⁵

The relaxation channel of the stress field related to the formation of fresh surface was studied most thoroughly. Many studies were devoted to the investigation of the kinetics of this process. Both the simplest regularities of coarse grinding (see Khodakov's monograph⁶) and more advanced models of fine grinding were considered which take into account the pulsed character of the mechanical impact and the effect of mechanical activation on the formation of fresh surface.^{7–11} These models have a formal character and are far from being capable of describing all experimental results, particularly those derived from studies of compounds with anisotropic properties. Detailed investigation of the chemical properties of the fresh surface

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showed^{2,5,12} that MCA of silicon, germanium, tin and magnesium oxides leads to the formation of different centres on their surfaces which have predominantly a radical nature. Interactions of these centres with various gases were described. The data obtained may be used for the prediction of processes occurring in the synthesis of catalytic systems and modification of their surfaces.

Yet another general channel of relaxation of the stress field is the formation of defects of the crystal structure and the exit of these defects onto the surface of crystallites. Numerous studies systematised in monographs^{1,3,4} showed that it was the formation of defects rather than fresh surface, that was the cause of higher, MCA-induced reactivities and catalytic activities of compounds. There is a suggestion (based on indirect data) that it is the defects of the crystal structure that are the catalytically active centres. In our opinion, in order to elucidate the effect of MCA on the catalytic activity, it is necessary to relate physicochemical features of defects to the nature of the catalysis considered as a sequence of chemical transformations of the catalyst and reagents.

The process of formation of defects has a thermodynamic nature: the system tends to minimise its free energy, while the localisation of the excess energy on defects is thermodynamically more advantageous than the regular distribution of elastic stresses over all the bonds of the crystal lattice. The appearance of defects is, as a rule, accompanied by changes in the electronic properties of activated compounds. For example, electronic levels are formed in the forbidden bands, the forbidden bands become narrower, the conductivity electrons appear in semiconductors, and the electron-donor properties are enhanced in semiconductors and dielectrics. The electronic theory of catalysis considers the influence of all these changes on the catalytic properties.

These are the basic channels of relaxation of the field of stresses arising upon mechanical impact on solids. Other emissive phenomena also take place; however, their influence on the catalytic properties and peculiarities of the synthesis of catalysts is not very obvious, and we will consider them henceforth only where necessary.

Studies devoted to the investigation of the effect of mechanical treatment on catalysts may be divided into three groups. In the first group the MCA effect is used for the synthesis of catalytic systems: in the second group the effect of MCA on the catalytic properties of compounds is dealt with and in the third group catalytic reactions under MCA conditions are considered.

II. Synthesis of catalytic systems

The methods of mechanochemistry can be used for both synthesis of catalysts, supports and sorbents and control of their performance.

One of the first examples of the systematic and purposeful use of MCA for the preparation of catalysts is the preparation of a polymerisation catalyst based on titanium and aluminium chlorides. It was found that grinding of titanium(III) chloride in a ball mill increases its catalytic activity in the propylene polymerisation.¹³ It turned out that in this case the α - and γ -TiCl₃ phases pass to the δ -modification, which is more active in this reaction.¹⁴ Aluminium–titanium chloride catalysts are prepared by joint grinding of either metallic aluminium and TiCl₄¹⁵ phases or titanium and aluminium chlorides,^{16,17} or the chlorides with the addition of trialkylaluminium.¹⁸ In all probability, this technological technique was discovered purely empirically, and its scientific substantiation was started only after the publication of the corresponding patents.^{15–18} The processes occurring during mechanical treatment of catalysts were described in Refs 19–21. Somewhat later, an analogous study of titanium–magnesium chloride catalysts was carried out.^{22–24} Summing up the results obtained, one can state that upon MCA of mixtures of TiCl₃ with AlCl₃ and TiCl₄ with MgCl₂ an interaction between the components takes place. In the former case, this leads to the formation of solid solutions with the structure of δ -TiCl₃, while in the latter case

titanium chloride is fixed on the surface of magnesium chloride. Discrepancy between some results should be noted: the catalyst prepared by joint activation of titanium and magnesium chlorides possesses high activity according to Kashiwa,²² while Zakharov *et al.*²⁴ found that it is not very active, although the conditions and duration of activation were similar in both studies.

Systematic studies on the application of MCA for the preparation of catalysts were carried out at the Ivanovo Institute of Chemical Technology. These studies were aimed at solving the problem of intensification of the interaction between solids and solutions containing other components of the catalysts. Mechanical treatment accelerated the interaction of iron, zinc and aluminium oxides with a solution of chromic acid.^{25–27} Upon treatment of aluminium oxide in an ammonium-carbonate solution of zinc,²⁸ of α - and γ -aluminium oxides²⁹ and of magnesium oxide³⁰ in an ammonium-carbonate solution of copper, sorption of ions from the solution onto the surface of the solid component was observed. This technological approach both favoured the interaction of components and allowed regulation of some operational properties of the catalysts: their catalytic activities, strength and mouldabilities. The activities of chromium catalyst in the methanol synthesis,²⁷ of complex oxide and magnesium–copper catalysts in the vapour conversion of CO,^{29,30} of aluminium–nickel catalyst in the vapour conversion of hydrocarbons³¹ increased. The enhancement of the strength of iron–chromium,²⁶ aluminium–copper–zinc–chromium²⁹ and aluminium–nickel³¹ catalysts, zinc–aluminium spinel and aluminium oxide used as supports^{28,29} was also observed. In addition, α -aluminium oxide acquired mouldability by the extrusion method, which allowed the preparation of granules of complex shape.³²

Studies aimed at the development of a sulfur sorbent were carried out at the same Institute. Dispersion of zinc oxide in solutions of carboxymethylcellulose and poly(vinyl alcohol) enhanced its mouldability by the extrusion method, increased its specific surface and sorption capacity with respect to sulfur-containing compounds.³³ An analogous effect was achieved upon dispersion of zinc oxide with aluminium oxide in an ammonium-carbonate solution.³⁴ According to Shirokov and Il'in,²⁸ the enhancement of the sorbent strength results from the hydration of the surface of aluminium oxide and formation of zinc aluminate, which plays the role of a binding agent. Treatment of zinc oxide in a planetary or vibratory mill led to an increase in its static and dynamic sulfur sorption capacity and enhancement of its cleavage strength and abrasion resistance.^{35,36} Based on these studies, a technology of production of a sulfur absorbent was developed.³⁷

The method of MCA was applied for the preparation of catalysts of deep oxidation used for the after-burning of flue gases. Studies by Bulgarian investigators were aimed at the enrichment of the surface of cobalt oxide with copper oxide owing to local overheating arising during MCA.^{38,39} Upon treatment of a mixture of cobalt and copper oxides, the copper oxide phase disappeared as a result of formation of a mixed oxide compound on the surface.³⁸ Comparison of different techniques of grinding of a mixture of oxides (in a planetary or vibratory mill, in a mechanical mortar) showed that the use of the vibratory mill is the most efficient.³⁹ Presumably, the copper ions are incorporated into the voids in the layer of the cobalt cations. An attempt was made to perform the mechanochemical synthesis of analogous systems using magnesium, zinc and manganese oxides⁴⁰ instead of copper oxide; however, these oxides did not interact in a vibratory mill. The cobalt–copper oxide catalysts prepared using MCA possessed higher activities in the CO oxidation and were more resistant to poisoning with sulfur dioxide^{38,39} than the catalysts obtained by conventional methods.

Massive copper and cobalt oxides are efficient catalysts of deep oxidation. However, practical application of these oxides is problematic because it is difficult to mould them. This problem may be solved by subjecting the oxides to a short-time MCA in a planetary mill before moulding.^{41–43} The authors relate the

positive effect to hydration of the surface of copper oxide upon interaction of a mechanically activated oxide with water^{41, 43} and to changes in the morphology of cobalt oxide particles.⁴¹

The use of MCA for the synthesis of lanthanum cobaltites and manganites proved to be successful.^{44, 45} Activation of mixtures of oxides and carbonates made it possible to reduce the temperature of formation of the corresponding perovskites by 250–300 K; the interaction at lower temperatures was more complete when the initial components were in the form of carbonates. As regards the specific surface and catalytic activity, the catalysts prepared using MCA were superior to the analogous systems obtained by traditional ceramic technology and were close to the catalysts prepared by the co-precipitation method; the advantage of the MCA consists in the absence of deleterious wastes.

The preparation of skeletal catalysts is very energy-consuming since the initial alloys of the corresponding metals with aluminium are obtained by the pyrometallurgical method. Besides, definite difficulties are associated with the completeness and rate of aluminium leaching. The use of MCA solves both these problems.

The beneficial influence of MCA on the properties of skeletal nickel was reported for the first time over four decades ago.⁴⁶ Treatment of an aluminium–nickel alloy in a vibratory mill increased the activity of the catalyst obtained after leaching in the reactions of cyclohexene hydrogenation and propan-2-ol dehydrogenation. Comparatively recently, methods were developed for the preparation of nickel–aluminium alloys by the so-called ‘mechanical alloying’, *i.e.* by mechanochemical activation of a mixture of powders of nickel and aluminium metals.^{47, 48} The use of ‘mechanical alloys’ makes it possible to increase the degree of aluminium leaching and to prepare Raney catalysts which are more active in the reactions of hydrogenation of phenylacetylene, potassium maleate and nitrobenzene.^{47, 49, 50} The skeletal catalysts prepared from the alloys obtained by the ‘mechanical alloying’ method may have a more complex composition and contain modifying additives.⁵¹ It should be noted that not any composition of the ‘mechanical alloys’ makes them advantageous. Thus the pyrometallurgical alloys containing > 80% of aluminium are better leached and ensure higher catalytic activity. The advantages of MCA are most clearly manifested in the regeneration of worked-out skeletal catalysts: its use for the preparation of ‘mechanical alloys’ makes it possible not only to restore the properties of skeletal nickel but also to achieve the activity several times higher than that before regeneration.⁵² The higher activity of the catalysts prepared from ‘mechanical alloys’ is possibly explained by the fact that after leaching nickel passes to a metastable state with the structure NiAl, whereas leaching of pyrometallurgical alloys leads to the formation of the face-centred cubic lattice.⁵³

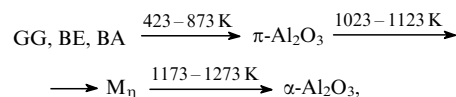
The ‘mechanical alloying’ method was also used for the preparation of hydrides of intermetallic magnesium compounds.⁵⁴ The ‘mechanical alloys’ are hydrogenated more easily than the pyrometallurgical ones, and hydrogen present in the hydrides obtained is more mobile. Hydrides of magnesium intermetallics proved to be efficient hydrogenation catalysts.⁵⁵ Compared to conventional catalysts, their advantage is particularly noticeably manifested in the reactions of selective hydrogenation of alkynes and dienes to alkenes. Thus the hydride with composition Mg₂FeH₆ provides a nearly 100% selectivity of hydrogenation of butadiene to butenes,⁵⁶ while Mg₂CoH₅ ensures the 100% selectivity of hydrogenation of acetylene to ethylene.⁵⁷ It should be noted that such a high selectivity in these reactions is reached on none of the known traditional catalysts. Preparation of hydrides through the ‘mechanical alloying’ stage is a waste-free energy-saving method which was used for the synthesis of new catalytic systems, *e.g.*, Mg₂FeH₆, Mg₂CoH₅ and Mg₃CoH₅.

The application of MCA for the preparation of iron–potassium dehydrogenation catalysts is described in sufficient detail in the literature. These catalysts are traditionally obtained by mixing iron oxide with potassium carbonate and potassium silicate. Thermal treatment of the paste obtained in water vapour leads

to the formation of the active component, *viz.*, potassium ferrite. Pretreatment of iron oxide in a disintegrator makes it possible to reduce the temperature of its reaction with alkali metal carbonates, to increase the yields of the corresponding ferrites and the rates of their formation. Higher degrees of conversion of ethylbenzene to styrene and a higher selectivity of styrene formation are reached⁵⁸ on the catalysts obtained from iron oxide treated in a disintegrator. Both these parameters are improved as the specific energy of treatment is increased.^{59, 60} In addition, such catalysts are better mouldable and possess higher strength.⁵⁹ Upon treatment of a mixture of iron oxide and potassium carbonate in a planetary mill, potassium ferrite is formed directly in the drum.⁶¹ If dehydrogenation is performed with the catalyst obtained after thermal treatment of a mixture activated in water vapour, the process begins at 670 K, whereas on the initial catalysts it starts only at 800 K. The mechanically activated catalyst exhibits an increased activity until 880 K at which it drops to the activity level of the initial specimen, which is associated with the annealing of defects in the crystal structure.⁶¹

Numerous studies were devoted to the use of MCA for the preparation of alumina-based catalysts and supports. Shirasaki *et al.*⁶² showed that grinding of corundum in water facilitates its formation; analogous data were obtained later by Il'in *et al.*³² The mouldability of alumina increases after MCA of the initial aluminium hydroxide.⁶³ In this case the resulting alumina is not inferior in its strength and sorption properties to the oxide formed from precipitated aluminium hydroxide the production of which provides large volumes of wastes. The possibility of regulation of some operational properties of catalysts with the aid of MCA was noted.^{32, 62, 63}

The possibilities of the use of MCA for the preparation of alumina-based catalysts and supports based on aluminium oxide are described in more detail in a series of papers from the Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences. Transformations of aluminium hydroxide in the course of MCA and during subsequent treatments were studied in detail. Upon activation of hydrargillite, grinding of crystals, shift of hydroxylic packs, cleavage of crystals into plates and dehydration with formation of molecular water which remains in the bulk among activation products occur.^{64–66} Analogous processes also take place upon MCA of bayerite.⁶⁷ The maximum quantity of excess energy accumulated in hydrargillite is 33 kJ mol^{–1}. This value is reached at the thickness of plates commensurable with the size of the unit cell of hydrargillite;⁶⁸ in this state hydrargillite manifests its maximum chemical activity. In studies of thermal transformations of activated hydrargillite, a new state of alumina was revealed and denoted as π -Al₂O₃.^{69, 70} This is characterised by the presence of aluminium cations in the pentacoordinated state. The structure of this oxide was established, and it was found that π -Al₂O₃ is capable of dissociative chemisorption of ammonia.⁷¹ Thermal transformations of all aluminium hydroxides subjected to MCA proceed in the same manner:⁷²



where GG, BE and BA are hydrargillite, boehmite and bayerite, respectively; M_η is the spinel-like phase of alumina.

On the other hand, non-activated aluminium hydroxides are transformed into corundum each in its own mode which is more complex than that considered above. It should be noted that the temperature of phase transition of activated hydroxides into corundum is 200 K lower than that of non-activated ones.⁷²

Detailed investigation of the processes which occur during MCA of aluminium hydroxides has allowed the development of techniques for the preparation a wide range of alumina-based catalysts, supports and sorbents. Thus depending on conditions, hydration of activated hydrargillite and π -Al₂O₃ leads to the formation of bayerite or pseudoboehmite from which different

aluminas are formed after thermal treatment.⁷³ The mechanism of hydration of the hydrargillite and π - Al_2O_3 MCA products has been established.^{74, 75}

Methods for the preparation of hydroxyaluminates of a number of divalent metals on the basis of the products of MCA of aluminium hydroxides were developed. Interaction of activated hydroxides with solutions of magnesium and zinc salts or with zinc oxide leads to the formation of the corresponding hydroxyaluminates.^{76–78} Under the same conditions, π - Al_2O_3 also enters into analogous interactions.⁷⁷ Presumably, hydroxyaluminates are formed through the stage of intercalation of salts.^{77, 78}

Yet another field of application of activated aluminium hydroxides is the synthesis of various aluminosilicates. In the MCA of kaolinite, processes analogous to those revealed in the activation of hydrargillite occur, *viz.*, shift and turn of layers as well as dehydration with the formation of molecular water remaining within the compound's structure.⁷⁹ In contrast to MCA of hydrargillite, mechanical activation of kaolinite does not alter the pathways of its thermal transformations.⁸⁰ The initial stage of thermal treatment includes formation of metakaolinite containing pentacoordinated aluminium cations.^{70, 80}

Upon MCA of a mixture of hydrargillite and silica gel, hydrated aluminosilicate is formed^{81, 82} from which an aluminosilicate spinel is formed first upon heating and then mullite. A non-activated mixture undergoes transformations which differ in many aspects. By varying conditions of hydration and thermal treatment of activated mixtures of hydrargillite and silica gel, it is possible to obtain amorphous aluminosilicates, kaolinite, montmorillonite, aluminosilicate spinel of high purity and mullite with large specific surface and without admixtures of corundum and cristobalite.⁷³ Furthermore, zeolites of types A, X, Y were obtained,^{73, 83} and the possibility of synthesis of over 100 other zeolites is predicted,⁸⁴ *i.e.*, good prospects are open for the development of little-waste methods for the preparation of zeolites.

Some aluminosilicates were synthesised using the so-called 'soft mechanochemical synthesis',⁸⁵ which involves MCA of hydrated or moist mixtures. It is suggested that in this case conditions are close to hydrothermal ones. The use of this method allows preparation of mullite without admixtures of other phases, a number of other aluminosilicates, as well as aluminates, titanates, zirconates, tungstates and vanadates of alkaline-earth metals. According to Avvakumov,⁸⁵ the method of 'soft mechanochemical synthesis' may be used for performing acid–base reactions proceeding with liberation of water.

New methods, including MCA, were developed for the synthesis of heteropolyacids (HPA) and catalysts based on them. A broad spectrum of HPA was obtained using mechanical activation of molybdenum and tungsten oxides and their mixtures with vanadium, silicon, aluminium and iron oxides. The most successful proved to be the use of MCA for the preparation of phosphomolybdic and phosphomolybdenovanadic HPA,^{86–89} in particular high-purity $\text{H}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$ and $\text{H}_{3+n}\text{PMo}_{12-n}\text{V}_n\text{O}_{40}$ with $n = 0–4$. The process is characterised by the total absence of deleterious wastes and flue gases, the time of synthesis is substantially reduced, energy consumption is decreased, losses of expensive raw materials are precluded, fire-hazard stages are absent, while the yield of HPA reaches the quantitative level.

When developing methods for the preparation of HPA, we revealed new oxide compounds of molybdenum and vanadium in the system $\text{V}_2\text{O}_5\text{--}n\text{MoO}_3$.⁹⁰ It is their formation that is the reason for such a smooth synthesis of HPA. Reactions of compounds of the system $\text{V}_2\text{O}_5\text{--}n\text{MoO}_3$ with phosphoric acid and its salts under conditions of MCA lead to the formation of HPA with composition $\text{H}_{3+n}\text{PMo}_{12-n}\text{V}_n\text{O}_{40}$, where $n \geq 3$, or their salts.⁸⁷ Apparently, an important role in these reactions is played by water of crystallisation since activation under the same conditions of a mixture containing anhydrous phosphates does not lead to the formation of HPA salts.

A waste-free method for the preparation of a catalyst for L-sorbose acetonation (one of the stages in the synthesis of vitamin C) was developed.⁸⁹ The catalyst is a mixture of phosphomolybdic heteropolyacids and provides higher yields of isopropylidene-L-sorbose than does oleum, which is normally used for this purpose, and precludes harmful acidic wastes. Mechanochemical activation is also used for the regeneration of the catalyst after isolation of the target product.⁸⁹

The application of MCA for the synthesis of nickel catalysts of decomposition of hydrocarbons proved to be rather effective. The reaction proceeds with the elimination of hydrogen and formation of filamentous carbon which is a material possessing specific, and in a number of cases, unique, physicochemical properties. Catalysts for these reactions are traditionally obtained by co-precipitation from solutions of nickel, copper and aluminium salts. MCA of nickel oxide or its mixtures with other oxides together with compounds of lamellar structure (magnesium and aluminium hydroxides, graphite) produces more efficient catalysts of decomposition of hydrocarbons than those obtained by co-precipitation.^{91–93} They operate for a long time without losing their activities, which provides higher degrees of transformation, *e.g.*, of methane. This makes cost-effective the production of hydrogen from hydrocarbons. The carbonaceous material formed can be used as a sorbent, a support for catalysts and as a catalyst.

Besides synthetic purposes, MCA is also used for improving certain operational characteristics of catalysts and supports. Thus treatment of a suspension of zeolite in a bead mill in the presence of surfactants made it possible to increase its strength.⁹⁴ Treatment of aluminium hydroxide in a vibratory mill facilitates its moulding and enhances the strength of granules of the final product.⁶³ As noted above, analogous results were obtained upon treatment of iron–chromium²⁶ and aluminium–zinc²⁸ catalysts, catalyst of vapour conversion of CO ,²⁹ aluminium, zinc, copper and cobalt oxides.^{34, 35, 41–45} The reasons for the increase in the strength of a phosphate catalyst of dehydrogenation resulting from the application of MCA were considered by Molchanov and Goidin. In the non-activated catalyst processes of baking, phase transition and recrystallisation of calcium phosphate occur⁹⁵ at virtually the same temperature. The last two processes induce mechanical stresses in the catalyst pellets which decrease their strength. Prior MCA reduces the phase transition temperature by 300–350 K and favours the completion of recrystallisation before the beginning of baking, which enhances substantially the strength of pellets.

Modification can also occur as a result of changes in sorption properties of a specimen due to grafting of various groups, formation of fresh surface and outcrops of defects to the surface. Mechanochemical grafting is used for the preparation of fillers for rubbers and plastics (see, *e.g.*, Ref. 96). We failed to find in the literature any examples of this kind of modification of surfaces of catalysts, supports or sorbents, though, in our opinion, this method is promising. However, the effect of formation of fresh surface upon MCA is used for the preparation of catalysts.^{25–30} The influence of defects in the crystal structure on properties of the surface was also revealed.^{97, 98} Mechanochemical activation of a number of oxide supports leads not only to the increase in their sorption capacity but also to a substantial decrease in the temperature of reduction of supported salts to metals and also to a higher catalytic activity of supported nickel in the ethylene hydrogenation. Data on the use of MCA for the preparation of catalysts are presented in Table 1.

We made an attempt to generalise the regularities of mechanochemical synthesis, *i.e.*, the interaction of compounds directly in the mill without any additional treatment. The mechanochemical synthesis occurs in the cases where the reagents have similar crystal structures; in the acid–base interaction, where one of the reagents is a strong acid or base (such a process is considered in sufficient detail by Avvakumov⁸⁵); in the formation of pseudomelts where an intense mechanical stirring can increase the

Table 1. Application of MCA for the preparation of catalysts.

Initial products	Final product obtained or the result	Apparatus for MCA	Additional effects	Ref.
α -TiCl ₃ , γ -TiCl ₃	δ -TiCl ₃	BM	increased activity in the propylene polymerisation	13, 14
TiCl ₃ + AlCl ₃ + R ₃ Al	δ -TiCl ₃	"	—	18
TiCl ₃ + AlCl ₃	solid solution with δ -TiCl ₃ structure	"	increased activity in the ethylene polymerisation	19–21
TiCl ₄ + MgCl ₂	fixation of TiCl ₄ on the MgCl ₂ surface	"	the same	22–24
α -Fe ₂ O ₃ or α -Al ₂ O ₃ + H ₂ CrO ₄ , Fe ₂ O ₃ + H ₂ CrO ₄	catalysts of vapour conversion of CO	BdM	increased activity, enhanced strength	25, 26
ZnO + H ₂ CrO ₄	catalyst of methanol synthesis	—	increased activity	27
Al ₂ O ₃ + Zn ²⁺ in ACS	sorption of Zn ²⁺ , formation of ZnAl ₂ O ₄	BdM	increased strength of the catalyst for desulfurisation	28
H ₂ CrO ₄ + Al(OH) ₃ + ZnO + + CuCO ₃ ·Cu(OH) ₂	catalyst of vapour conversion of CO	—	increased activity	29
MgO + Cu ²⁺ in ACS	the same	—	the same	30
CuAl ₂ O ₄ + ethanol or acetone solution	improved quality of binding agent	—	Enhanced strength	31
α -Al ₂ O ₃	possibility of moulding by extrusion	BM, VM	—	32
ZnO + CMC (or PVA or PEG)	sulfur adsorbent	USD	improved capability for moulding, increased sulfur capacity	33, 37
ZnO + Al ₂ O ₃ in ACS	the same	—	enhanced strength, increased sulfur capacity	34, 35
ZnO	"	VM, PM	the same	36
CoO + CuO	catalyst of after-burning	the same	increased activity in CO oxidation, resistance to poisoning with SO ₂	38, 39
CuO, Co ₃ O ₄	improved capacity for moulding by extrusion	PM	increased CuO activity in butane oxidation	41–43
La ₂ O ₃ + Co ₃ O ₄ , La ₂ (CO ₃) ₃ + CoCO ₃ ·Co(OH) ₂	LaCoO ₃ (catalyst of after-burning of flue gases)	"	—	44
La ₂ O ₃ + Mn ₂ O ₃ (or MnO ₂ or Mn ₃ O ₄)	LaMnO ₃ (catalyst of after-burning of flue gases)	"	—	45
Al–Ni (alloy)	Ra/Ni	VM	increased activity in cyclohexene hydrogenation	46
Ni + Al	alloys, precursors of Ra/Ni	PM	increased activity in hydrogenation reaction	47–50
Ni + Al + M (M = V, Cr, Mn, Fe, Co, Mo, W)	modified Raney nickel	"	the same	51
Ra/Ni (used) + Al	Ra/Ni	"	"	52
Mg + Ni (or Fe or Co)	alloys, precursors of intermetallic hydrides	"	high selectivity of hydrogenation of dienes and acetylenes to alkenes	55–57
M ₂ CO ₃ + Fe ₂ O ₃ (M = K, Rb, Cs)	catalyst of ethylbenzene dehydrogenation	DS	Increased activity, enhanced strength	58–60
Aluminium hydroxides	various crystalline modifications of Al ₂ O ₃	PM	—	64–75
	formation of hydroxyaluminates through intercalation of Mg and Zn salts	"	—	76–78
Aluminium hydroxides + SiO ₂	aluminosilicates, zeolites	"		73, 81–85
MoO ₃ or its mixture with V ₂ O ₅	heteropolyacids	"	total absence of waste	86–89
NiO + Al(OH) ₃ or CuO + Mg(OH) ₂	catalysts of decomposition of hydrocarbons to C and H ₂	"	high activity and stability	91–93
Ca–Cr–Ni-phosphate catalyst IM-2204	regulation of the processes of crystallisation and baking	"	enhanced strength	95
ZnO, TiO ₂ , Al ₂ O ₃ , ZnAl ₂ O ₄	changes in sorption properties	"	decrease of the temperature of reduction of deposited salts, increased activity of supported metals	97, 98

Note. Abbreviations: ACS, ammonium-carbonate solution; CMC, carboxymethylcellulose; PVA, poly(vinyl alcohol); PEG, poly(ethylene glycol); Ra/Ni, Raney nickel; BM, ball mill; BdM, bead mill; UD, ultrasonic disintegrator; VM, vibratory mill; PM, planetary mill; DS, disintegrator.

mobilities of molecules of at least one of the reagents to the level of their mobilities in a melt.

But even if no reactions occur in the mill, MCA all the same facilitates substantially other stages of the catalyst's preparation. This is determined by changes in the thermodynamic potentials due to the formation of defects, changes in electronic properties, appearance of fresh surface, *etc.* The most substantial effect is

observed for high degrees of homogenisation of mixtures of reagents, which facilitates appreciably mutual diffusion.

The interaction of components in the MCA is determined by different properties of solids, such as chemical compositions and reactivities, hardness and fragility, crystal structure and bond strength, melting temperatures and others. For this reason, there is no integral theory or any versatile reference points so far which

would make it possible to predict the result of joint MCA of at least binary systems. So far one can be satisfied solely with some specific speculations.

In our opinion, a kind of activated state arises in the MCA of mixtures of compounds. Relaxation after discontinuing of load results either in the formation of new compounds or in the return to the initial compounds which are however characterised by higher dispersion and excess energy. Naturally, the former is only possible in the absence of thermodynamic restrictions for the reaction of components. But even if the formation of new compounds is possible in principle, one cannot be sure that this possibility is realised under the MCA conditions. A substantial importance has the transition of at least one of the compounds subjected to activation to the viscous-fluid state. Here, it is possible to draw an analogy with the processes of adhesion of liquids or melts or mixing of liquids where several interacting components pass to the viscous-fluid state. In this state, the number and area of contacts between reagents increase substantially, and in the case of chemical affinity, interaction between them becomes possible. If we continue to draw an analogy with the processes of adhesion, then the phase passing to the viscous-fluid state should be called adhesive, while the other phases should be termed substrates. Correct methods for the calculation or determination of thermodynamic potentials in the adhesion or mixing of melts could also be used for predicting the possibility of the occurrence of mechanochemical synthesis. In particular, one can use the known expressions for the adhesion and cohesion works (W_{ad} and W_c , respectively), *i.e.*, the energies that should be spent for the separation of the adhesive and substrate over the interface or for the separation of components of the adhesive to an infinite distance.

$$W_{ad} = \gamma(1 + \cos \theta),$$

$$W_k = 2\gamma,$$

where γ is the surface energy of adhesive (in our case, for the phase which passed to the viscous-fluid state), θ is the angle of wetting.

In the mechanochemical synthesis, the following processes presumably take place successively. First, one or several components pass to the viscous-fluid state. As this process is not momentary, grinding and activation of other components occur simultaneously. After formation of the viscous-fluid phase its adhesion on the surface of other components occurs. If $W_{ad} > W_c$, total wetting takes place. This condition is always fulfilled in the case of formation of chemical bonds between the adhesive and substrate. As a rule, the adhesion forces are stronger than the cohesion forces, *i.e.*, than the forces of intermolecular attachment in the viscous-fluid phase. Because of this, relaxation of stresses in repeated loading of substrate–adhesive particles is manifested in the cleavage of bonds inside the viscous-fluid phase rather than in the separation over the interface. The separated part of the adhesive wets the free surface of the substrate which is formed as a result of grinding. Mechanical loading of the substrate phase with the fixed adhesive should lead to phenomena analogous to the effect of adsorption-induced dispersion since the surface energy of the interface (an analogue of the surface tension for solids) tends to a minimum upon complete wetting. Intensification of the dispersion processes leads to an increase in the surface of wetting. Atoms and molecules belonging to the interface possess high mobilities due to both the viscous-fluid state and the external mechanical impact. This favours an increase in the rates of mutual diffusion. All the above-mentioned factors result in the formation in MCA of lamellar structures either at the molecular level, as in the system V_2O_5 – MoO_3 , or at the micro-level, as in the mechanical alloying of metals⁹⁹ or upon application of metals onto solid supports by means of MCA of their mixtures^{100, 101} (see below).

If complete wetting does not occur, *i.e.*, none of the interacting phases passes to the viscous-fluid state, the phases undergone activation are dispersed and their particles several nanometres in

size prove to be homogeneously mixed, which facilitates substantially the diffusive transfer which is necessary for the interaction of components during subsequent treatments of activated mixtures. Owing to the changes in thermodynamic potentials, the reactivities of components increase in both cases.

Thus, MCA can successfully be used for the direct synthesis of catalytic systems, for facilitating the interaction of components during further treatments (calcination, hydration, sorption, *etc.*) and for the improvement of performances of the products obtained (their mouldability, strength, sorption and catalytic properties). The most important advantage of the mechanochemical methods is the possibility to develop wasteless technologies of the production of catalysts based on them. The importance of the development of wasteless methods is determined by the fact that at present the world production of catalysts is estimated at hundreds of thousands of tons. A considerable part of catalysts is obtained using precipitation methods, which are accompanied by large volumes of wastes. Over half the elements of the Periodic system, including highly toxic ones, are used in the production of catalysts and supports. It may be said without exaggeration that the preparation of catalysts, supports for them and adsorbents are environmentally most deleterious industries. The application of wasteless methods can not only improve the environmental situation in areas of production of catalysts but also decrease their cost owing to lower expenses for neutralisation of wastes. Examples of successful replacement of precipitation methods by wasteless methods based on the use of MCA are the preparation of supports and catalysts based of alumina^{64–84} and the synthesis of catalysts of decomposition of hydrocarbons.^{91–93} The use of wasteless methods of HPA synthesis is environmentally friendly.^{86–89}

Yet another advantage of mechanochemical methods is the decrease in energy consumption. This is achieved owing to the reduction of temperature and time of interaction of components. Thus the preparation of aluminides of several metals, which are precursors of skeletal catalysts, by pyrometallurgical methods requires heating to melting temperatures and in some cases multiple alternations of fusion and grinding are needed. Alloying under the MCA conditions is completed within a few minutes, and in this case the possibilities of variation of the composition of alloys are substantially extended.^{47–53} The same advantages are realised in the preparation of hydrides of intermetallic compounds from ‘mechanical alloys’.^{54–57} Heteropolyacids are formed by reactions of metal oxides with phosphoric acid at its boiling temperature (~ 373 K) for several hours, whereas the application of MCA makes it possible to decrease the temperature to 323–343 K and the reaction time to a few minutes (some HPA can be prepared at room temperature within a few seconds).^{86–89} There are numerous other examples of a substantial decrease in the temperatures of interaction of components and phase transitions. The reduction of energy consumption improves indirectly the environmental situation since energy production is one of the most deleterious for the environment.

With the use of MCA novel catalysts have been synthesised, including those never isolated earlier in the form of individual chemical compounds. Often such systems possessing unique catalytic and chemical properties cannot be synthesised by other methods. This is exemplified in the preparation of alumina π - Al_2O_3 ^{69, 70} and Raney nickel with the structure of the type $NiAl$,⁵³ as well as in the synthesis of hitherto unknown hydrides of magnesium intermetallides⁹⁹ and new compounds in the system V_2O_5 – MoO_3 .⁹⁰ The application of new catalytic systems prepared using MCA makes it possible to increase the efficiency of catalytic processes, which is often difficult or impossible to achieve by conventional methods.

Broad possibilities are opened by the use of MCA for the regulation of processes which occur in the course of formation of catalytic systems (crystallisation, baking, phase transitions, *etc.*). The temperatures of all these processes and their rates can be varied with the aid of MCA. This makes it possible to govern the

strength, parameters of a porous structure and the specific surface area of catalysts.

Mechanochemical modification of catalysts and supports is not described in sufficient detail in the literature. It is, however, clear that MCA increases the strength of specimens, improves their mouldability and regulates sorption properties. It should be noted that structures formed upon mechanochemical synthesis are non-equilibrium and possess increased reactivities, including those in the target reactions. This phenomenon will be considered in more detail below.

However, a broad range of issues has not been duly described as yet. Thus the possibilities of the use of short-living active sites for the modification of catalytic and sorption systems were not virtually studied. Few studies were devoted to the methods of mechanochemical grafting of various functional groups onto the surface of solids to be used in processes of sorption and catalysis. Potential possibilities of the methods of mechanochemistry are tremendous, as regards the search for novel catalytic systems hitherto unknown as chemical compounds. The list of similar topics could be continued but even those cited above are sufficient for becoming aware of the advisability of intensification of studies in this field.

III. Effect of mechanochemical activation on catalytic properties of compounds

1. Metal catalysts

Apparently, the effect of mechanical impact on catalytic properties of compounds was first revealed by Eckell¹⁰² who has compared the activity of nickel foil in the ethylene hydrogenation before and after rolling. The rolling led to a substantial increase in the nickel activity which decreased after annealing the foil at 473–573 K. Analogous results were obtained in studies of formic acid decomposition.^{103, 104} Correlation of the catalytic activities of the specimens studied^{102, 103} with the physical properties of mechanically treated metals made it possible to suggest that the catalytically active centres are dislocations.¹⁰⁵ This suggestion was confirmed later in numerous examples by Japanese investigators. It was shown^{106–112} that cold treatment of metals (twisting, rolling, moulding) increased the catalytic activity of copper, nickel, silver, gold and platinum in decomposition reactions of diazonium chloride, formic acid and hydrogen peroxide, dehydrogenation of ethanol, hydrogenation of cinnamic acid, oxidation of ethanol and *ortho*–*para* conversion of hydrogen. It was concluded that both dislocations and point defects are responsible for the increase in catalytic activity. Thermal annealing led in all cases to a decrease in activity to the level of activity of untreated metals; and properties of catalysts such as hardness, electroconductivity and thermo-EMF changed simultaneously. Many investigators^{106–112} relate this to the disappearance of defects.

The reasons for the increase in the catalytic activity of metals resulting from mechanical impact were elucidated in more detail in studies of the effect of treatment of nickel and cobalt powders in ball and vibratory mills on their activities in the hydrogenation of benzene and fats. An extreme dependence of cobalt activity on the time of treatment was revealed and the transition of the cubic form of metal to the hexagonal one was established.^{113, 114} Examination of a cobalt powder subjected to treatment in mills with subsequent heating, using a set of physicochemical methods, showed that the increase in the catalytic activity of the metal in benzene hydrogenation is determined by the presence of defects and a distorted crystal lattice, as well as by the density of defects.^{115–118} Deactivation of catalysts upon heating was associated with dislocation and annihilation of vacancies.¹¹⁸

A nickel powder treated in a ball mill increased its activity in the hydrogenation of benzene,^{113, 119} phenol and higher alcohols¹²⁰ and fats.¹²¹ Correlation of the nickel activity in the above-mentioned reactions with changes in its physicochemical properties suggests that the increase in activity is to a larger extent associated with disordering of the crystal lattice than to the

surface area increase.^{120, 121} In their completing study, the authors attempted to relate changes in the catalytic properties of mechanically activated nickel to changes in its crystal structure.¹²² Specific rate constants of hydrogenation of fats and *ortho*–*para* conversion of hydrogen were found to be linearly dependent on the number of distortions of the crystal lattice and the density and energy of dislocations. The activation energy of reactions was inversely proportional to the energy of dislocations.¹²² The data obtained would seem to provide an unambiguous proof that dislocations in metals are catalytically active centres. However, the method of determination of specific activities of catalysts used by the authors cannot unfortunately be regarded as correct. The rates of reactions were estimated from the degree of conversion referred to a unit surface. But the degree of conversion is an integral (as regards time and concentrations) magnitude and cannot serve as a measure of the catalytic activity. The models used for the determination of the number and density of dislocations were far from being perfect. Analogous drawbacks are also inherent in the above-cited studies by Japanese researchers.^{116–122} Nonetheless, all these publications made a substantial contribution to the understanding of the nature of the effect of mechanical impact on the catalytic activities of metals.

2. Oxide catalysts

The effect of mechanical treatment on the catalytic properties of oxide systems was revealed for the first time in studies of the catalytic activity of lead oxide in the decomposition of hydrogen peroxide as a function of time of treatment in a ball mill.¹²³ The effect of mechanical treatment on the activity of V₂O₅, Fe₃O₄ and Fe₂O₃ in the oxidation of sulfur dioxide was studied more than two decades later.^{124, 125} The dependence of the catalytic activity of vanadium oxide on the time of treatment has two maxima,¹²⁴ while the activities of both iron oxides pass through one maximum.¹²⁵ The increase in catalytic activity is presumed to be related to distortions of the crystal lattice rather than to a larger surface area. Mechanical activation of iron oxides was also used in the oxidation and vapour conversion of CO.^{126, 127} The dependences of the Fe₂O₃ activity on the treatment time has an extremal character in both reactions, whereas the same dependence for Fe₃O₄ is described by a curve with saturation. Fe₃O₄ subjected to mechanical treatment is more active than the industrial catalyst of vapour conversion of CO;¹²⁷ however, no satisfactory explanation of this effect has been given so far.

Mechanical treatment of vanadium and iron oxides leads to an increase in their adsorption capacity with respect to sulfur dioxide and hydrogen sulfide;^{124, 128, 129} the positions of the maxima of the catalytic activities and adsorption capacities virtually coincide on the time dependence curves.

An attempt was made to elucidate the reasons for the effect of mechanical activation on the catalytic properties of calcium and copper oxides in the decomposition of N₂O and *ortho*–*para* conversion of hydrogen.^{130–132} There is a quantitative dependence between the catalytic activity of calcium oxide in the decomposition of N₂O and the concentration of defects in the crystal lattice. This is evidenced by the same degree of decrease, resulting from thermal treatment, of both the catalytic activity and some parameters (determined by the X-ray diffraction method) which characterise the defectiveness of activated samples. The increase in the copper oxide activity is rationalised within the framework of the electronic theory of catalysis. It is presumed that as a result of mechanical treatment the conductivity of *n*-type passes to the conductivity of *p*-type, while the activity of the catalyst in the decomposition of N₂O is determined by the ease of electron transfer in elementary stages.¹³² Changes in the catalytic properties of copper oxide in the *ortho*–*para* conversion of hydrogen are related to magnetic properties,¹³¹ while no mention is made about electronic properties.

Mechanical treatment can not only increase, but also decrease catalytic activity. Examples of this type, though not numerous, are the decrease in the zinc oxide activity in the decomposition of

hydrogen peroxide and photooxidation of propan-2-ol after treatment in a ball mill.^{133–135} The activity of zinc oxide drops linearly as the degree of disorderliness of the crystal lattice increases. The activation energy of hydrogen peroxide decomposition on mechanically treated zinc oxide decreases with the increase in the number of paramagnetic centres which are edge dislocations.¹³⁶

The increase in the activity of zinc oxide, treated under analogous conditions, in the decomposition of hydrogen peroxide is related to a distortion of the crystal lattice.^{137–139} A comparative study of the effect of nickel and zinc grinding in a ball mill on the activation energy of hydrogen peroxide decomposition¹³⁹ made it possible to conclude that the differences observed are determined by the type of conductivity of these semiconductors possessing the *p*-type and *n*-type conductivities, respectively.

Changes in catalytic properties occur not only upon treatment in a mill, but also under other types of mechanical impact. Thus the effect of compacting pressure on the properties of a number of catalysts was reported.^{140–150} The accompanying changes in acidic properties of potassium hydrogensulfate and tungstic acid induce an increase in their activities in the acetylene polymerisation and propylene hydration, respectively.^{140–141} The activities of chromium-containing oxide catalysts in the dehydrogenation of alcohols^{142–148} and of an aluminium–cobalt–molybdenum catalyst in hydrogenolysis of thiophene^{149,150} show extremal dependences on the compacting pressure. The changes in catalytic activities are rationalised with the use of data on porous structures and variation of the interplanar distances. However, it should be noted that the methods used for the determination of the activity of catalysts in the studies cited are incorrect.^{140–150}

Yet another type of mechanical impact is the treatment of materials with shock waves. The activity of numerous simple and complex oxides as well as their mixtures in the CO oxidation increases after the application of shock waves.¹⁵¹ This is related to the appearance of anionic vacancies and other perturbations of the crystal structure. The increase in the titanium dioxide activity is not associated with the presence of paramagnetic centres Ti^{3+} and paramagnetic defects.¹⁵² It should be noted that upon application of shock waves appreciable admixtures of the reactor construction material are introduced into catalysts, and these admixtures can affect their catalytic properties.¹⁵¹ Therefore, it is not excluded that high activity of titanium dioxide observed by Golden *et al.*¹⁵² is explained by the presence of copper oxide compounds of which the reactor was made. By varying conditions of shock load one can regulate catalytic properties of fluorite;¹⁵³ not only an increase in the degree of transformation on this catalyst was observed, but also wide-range changes in the ratio of propan-2-ol dehydrogenation and dehydration rates.

Activation of supported catalysts is of definite interest. Thus treatment of a mixture of metallic nickel and quartz in a vibratory mill results in coating of quartz with nickel, and this makes it possible to reach a high rate of benzene hydrogenation.¹⁰⁰ The increase in catalytic activity is explained by distortions of the crystal lattice of nickel. Schulz *et al.*¹⁰¹ treated a mixture of nickel–ruthenium alloy and aluminium oxide in a similar manner. The system obtained was studied in detail by physicochemical methods; however, no data on its catalytic properties were reported. Of some interest is the preparation of alloys with non-equilibrium composition which preserve their thermal stabilities up to 673–773 K. Chromium, vanadium and molybdenum oxides supported on silica gel were also subject to mechanical treatment.^{154–156} Their catalytic activities in ethylene polymerisation,¹⁵⁴ propylene metathesis¹⁵⁵ and methane oxidation to formaldehyde¹⁵⁶ increased after activation in a vibratory mill in different media. Possible mechanisms of formation of active centres of these catalysts involving radical centres of silica were considered. Though, the authors do not provide any conclusive evidence of these mechanisms. A possible mechanism of the catalytic oxidation of methane is also discussed.¹⁵⁶ Of interest is the fact of an increase in the selectivity of formaldehyde formation

resulting from a virtually complete suppression of the reactions of deep oxidation of methane on activated catalysts; however, this effect is observed only at low degrees of methane conversion (1%–2%).¹⁵⁶ Unfortunately, in all studies the activity of deposited catalysts was determined without due account for the specific surface of the active component. In a number of cases, indeed, there are no corresponding methods, but they do exist for supported metals. Without knowledge of the specific surface of active component, it is impossible to establish the reason for the effect of mechanical activation on catalytic properties; furthermore, there is a risk of reaching conclusions which are opposite to the real situation.

Analysis of a large body of available experimental data allows one to avoid mistakes made in some works and to continue studies of the effect of mechanical treatment on catalytic properties of compounds at a more perfect level using modern methods. This concerns primarily the methods for the determination of catalytic activity. In the studies discussed below, the catalytic activity was determined, in our opinion, in the most correct manner, *viz.*, in the gradient-free (with regard to temperature and concentrations) conditions, while the reaction rates were referred to a catalysts unit surface. In addition, a set of modern research methods were used in these studies in order to determine the nature and concentration of defects formed in the MCA.

Oxides which are effective catalysts of deep oxidation were the subjects of studies. Activation of copper oxide in a planetary mill even for a few seconds increased 2–5-fold the specific rate of butane oxidation.^{43,157} Presumably, the reasons for this are structural perturbations in the subsurface layer and the increase in the surface concentration of Cu^+ ions, which are the centres of chemisorption.¹⁵⁷ On the contrary, cobalt oxide decreases its activity in the oxidation of butane,¹⁵⁸ and this is explained by the removal of excess oxygen in the course of mechanical treatment. A decrease in activity was also observed upon mechanical treatment of iron(III) oxide¹⁵⁹ having a defective structure. It is presumed that the treatment results in the disappearance of surface and subsurface defects with a local spinel symmetry. It was reported¹⁵⁹ that specific catalytic activity of $\alpha-Fe_2O_3$ depended almost linearly on the concentration of extended defects determined by the method of small-angle X-ray scattering. The graph which we plotted on the basis of these data (Fig. 1) confirms the conclusion made by the authors. Activation of manganese oxides induced a 2–5-fold increase in the specific rate of CO oxidation depending on the chemical composition of the oxide.¹⁶⁰ An increase in the activity of Mn_2O_3 is explained, as for Mn_3O_4 , by the appearance of extended defects. In this case, an increase in the oxygen content is also observed. The authors relate the appearance of active centres of Mn_2O_3 to the formation of steps on the faces $\langle 120 \rangle$, whereas the activity of MnO is believed to be associated with the formation of $\gamma-Mn_2O_3$ on the surface. Sadykov *et al.*¹⁶¹ have generalised and analysed the data on the effect of MCA on the defectiveness and reactivity of oxide catalysts of deep oxidation.

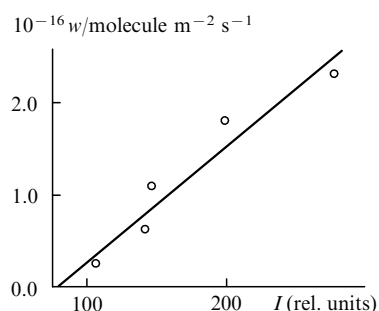


Figure 1. Dependence of the specific rate of CO oxidation on $\alpha-Fe_2O_3$ (w) on the integral intensity of small-angle scattering (I) (according to the data of Ref. 159).

In the MCA of zinc oxide the following three processes occur successively, *viz.*, accumulation of shear defects, relaxation of the structure resulting from grinding and agglomeration of particles formed upon grinding.¹⁶² Accumulation of defects is accompanied by the increase in the specific activity of the catalyst for the oxidation of CO; upon fissuring or breaking of crystallites over shear defects the activity returns to the preactivation level.^{163, 164} A catalytic act is supposed to involve oxygen chemisorbed at sites of the exit of shear defects onto the surface.¹⁶⁴ Accumulation of defects occurs in a very narrow range of activation times; apparently, it is due to the fact that the effect of activation was not revealed in the above-cited studies.^{133–136}

An unambiguous evidence of the role of defects as the centres responsible for the increase in catalytic activity was obtained in studies of titanium dioxide. Figure 2 shows the linear dependence of the specific rate of CO oxidation on TiO₂ on the concentration of planes of crystallographic shear.¹⁶⁵ To our knowledge, there are only three studies which revealed experimentally the quantitative dependence of the specific catalytic activity on the concentration of defects.^{122, 159, 165} Only this dependence may be regarded as a strict proof that defects are the active centres of catalysis. How-

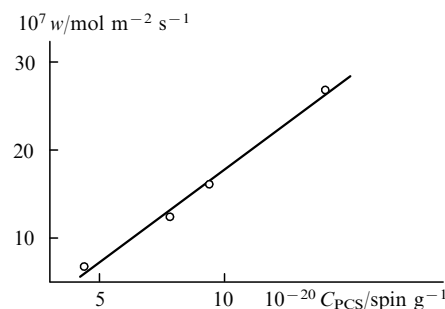


Figure 2. Dependence of the specific rate of CO oxidation on TiO₂ on the concentration of planes of crystallographic shear (C_{PCS}).

ever, Schrader *et al.*¹²² used an incorrect method for the determination of specific catalytic activity, and in this case such a conclusion cannot be regarded as correct. The data on the effect of mechanical impact on the activity of catalysts of different nature are presented in Table 2.

Table 2. The effect of MCA on catalytic properties of various compounds.

Catalyst	Reaction	Active centre	Ref.
Ni	hydrogenation of ethylene	—	102
	decomposition of formic acid	dislocations	103–105
Cu	decomposition of diazonium chloride	the same	106, 107
	dehydrogenation of ethanol	"	107
Ni	hydrogenation of cinnamic acid, dehydrogenation of ethanol, decomposition of H ₂ O ₂ , <i>ortho</i> – <i>para</i> conversion of hydrogen	vacancies, dislocations	108, 109
Ag	decomposition of formic acid, decomposition of H ₂ O ₂ , oxidation of ethanol	dislocations	110
Au	decomposition of H ₂ O ₂	the same	111
Pt	decomposition of formic acid, hydrogenation of cinnamic acid	point defects, dislocations	112
Co	decomposition of H ₂ O ₂ , hydrogenation of benzene	defects and distortions of the structure	113–118
Ni	hydrogenation of benzene	distortions of the lattice	113, 119
	hydrogenation of phenol and mixtures of higher unsaturated alcohols	the same	120
	hydrogenation of fats, <i>ortho</i> – <i>para</i> conversion of hydrogen	dislocations	121, 122
PbO	decomposition of H ₂ O ₂	—	123
V ₂ O ₅	oxidation of SO ₂ to SO ₃	distortions of the lattice	124
Fe ₂ O ₃ , Fe ₃ O ₄	the same	the same	125
	oxidation of CO	—	126
	vapour conversion of CO	distortions of the lattice	127
CuO	decomposition of N ₂ O, <i>ortho</i> – <i>para</i> conversion of hydrogen	defects of the lattice	130, 131
CaO	decomposition of N ₂ O	the same	132
NiO	decomposition of H ₂ O ₂	distortions of the lattice	137–139
KHSO ₄	polymerisation of acetaldehyde	new acidic centres	140
H ₂ WO ₄	hydration of propylene	new proton centres	141
Cr ₂ O ₃ + CuO or/and ZnO	dehydrogenation of Pr ⁱ OH	distortions of the lattice	142–148
TiO ₂ , ZnO, BaTiO ₃ , NiO, TiO ₂ + WO ₃ , TiO ₂ + Fe ₂ O ₃	oxidation of CO	anionic vacancies	151
TiO ₂	the same	distortions of the lattice	152
CaF ₂	dehydrogenation and dehydration of Pr ⁱ OH	—	153
Ni + SiO ₂	hydrogenation of benzene	distortions of the lattice	100
CrO ₃ + SiO ₂	polymerisation of ethylene	≡SiO [•] + Cr ⁿ⁺ ($n < 6$)	154
MoO ₃ + SiO ₂	metathesis of propylene	≡SiO [•] + Mo ⁴⁺	155
V ₂ O ₅ + SiO ₂	oxidation of methane to formaldehyde	—	156
CuO	oxidation of butane	surface Cu ⁺ ions	43, 157, 161
Co ₃ O ₄	the same	excess oxygen	158, 161
Fe ₂ O ₃	oxidation of CO	defects with a local symmetry of spinel	159, 161
MnO ₂ , MnO, Mn ₃ O ₄ , Mn ₂ O ₃	the same	extended defects, steps	160, 161
ZnO	"	shear defects	162–164
TiO ₂	"	planes of crystallographic shift	165

3. Annihilation of defects as a factor of deactivation of catalysts

In the process of operation, catalysts are known to lose gradually their activity and selectivity, to degrade, *etc.* The reason for deterioration of properties of catalysts, which can also be differently manifested in the use of systems subjected to MCA, were examined in detail.¹⁶⁶ The problem of the lifetime of systems with increased reactivities resulting from MCA has an independent significance and is fairly topical.

In a number of instances, the mechanism of the disappearance of defects resembles in many respects mutual annihilation of particles and antiparticles. For example, this seems to be the case of the interaction of dislocations with the counter-directed Burgers vectors of the same magnitude or the interaction of vacancies with the internodal ion. In virtually all of the studies cited in this section, a decrease in catalytic activity resulting from the disappearance of defects was noted. Most often, the annihilation of defects is induced by thermal annealing. This concerns both metal^{106–122} and some oxide^{123, 130, 138} catalysts.

The activity of mechanically activated copper oxide in the butane oxidation decreases when a specimen is stored for a long time and as a result of catalytic reaction.¹⁵⁷ In our opinion, this occurs due to processes which are analogous to those taking place in the course of annealing, although the rate of the disappearance of defects is substantially lower due to a decreased temperature. Sometimes, other factors are also found to play a role. Thus the degradation of crystallites of zinc oxide over shear defects leads to relaxation of the crystal structure.¹⁶² For iron oxide, a mechanism was proposed for the disappearance of defects due to the shear of layers.¹⁵⁹ The recovery of the initial stoichiometry of compounds can be yet another reason for deactivation. For instance, the removal of excess oxygen from cobalt oxide in the process of MCA leads to a decrease in its activity in the butane oxidation,¹⁵⁸ while the disappearance of the planes of crystallographic shear in titanium dioxide in oxidative media makes it less active in the oxidation of CO.¹⁶⁵ All these facts altogether gave us ground for supplementing the existing list of reasons for deactivation of catalysts¹⁶⁶ with one more factor, *i.e.*, annihilation of defects of the crystal structure.^{163, 167}

In some cases, mechanical treatment can lead to a complete and irreversible inactivation of catalysts. Thus mechanical treatment of zeolite FeZSM-5 destroys its crystal structure and leads to the total loss of activity in the phenol oxidation by dinitrogen oxide.¹⁶⁸ For the same reason, aluminium oxide loses its ability for coke formation after mechanical treatment,¹⁶⁹ which is a positive factor under the condition of preservation of useful properties by this material, *e.g.*, high sorption capacity.⁹⁷

It is commonly assumed that the defects disappear at sufficiently low temperatures, so the effect of increase in activity upon MCA cannot be used for practical purposes. However, there are many well known chemical processes which occur at temperatures substantially lower than the temperatures of annealing of defects. For example, skeletal catalysts prepared with the use of mechanical melting are effective in the hydrogenation reactions at temperatures of 373 K and below. The catalysts of deep oxidation preserve their elevated activities acquired upon MCA for at least tens of hours.¹⁵⁷ In a number of cases, annealing of defects requires unusually high temperatures. For example, the activity of iron–potassium catalyst in the dehydrogenation of *n*-butenes is decreased only upon heating to temperatures above 903 K,⁶¹ which is the operation conditions of an industrial reactor. Thus, the increase in the catalytic activity by MCA may be used for practical purposes, too.

4. Effect of mechanochemical activation on the selectivities of catalysts

Very few studies have been devoted to the investigation of the effect of MCA on the selectivities of catalysts. Treatment of molybdenum disulfide in a vibratory mill changes its selectivity in the thiophene hydrodesulfuration, the direction of this change

being dependent on the composition of the medium in which this treatment is carried out.¹⁷⁰ This is attributed to changes in the ratio of crystallographic facets possessing different catalytic properties. Upon grinding in heptane, the ratio of the surfaces of basal and lateral facets of molybdenum disulfide is 72 : 28, whereas upon grinding in air it is 5 : 95. At close degrees of thiophene conversion the ratios of concentrations of butane and butenes formed on these samples reach 0.7 and 3.0, respectively. In addition, the sample with a larger proportion of lateral facets is capable of sorbing a larger amount of hydrogen, chemisorption beginning at substantially lower temperatures. The use of fluorite subjected to MCA increases the selectivity of acetone formation from propan-2-ol.¹⁵¹ Treatment of a suspension of VOHPO₄ in ethanol in a planetary mill leads to the increase of the portion of the surface formed by the facets {001} of vanadium hydrogen-phosphate, which are transformed into the facets {100} of vanadyl pyrophosphate upon thermal treatment.¹⁷¹ The elevated content of the latter favours an increase in the selectivity of maleic anhydride formation upon oxidation of *n*-butane. We observed a decrease in the selectivity of butadiene formation upon dehydrogenation of *n*-butenes on a mechanically activated iron–potassium catalyst.⁶¹ Iron carbide Fe₃C subjected to MCA increases the selectivity of formation of hydrocarbons C_{*n*}, where *n* ≥ 2, and decreases the alkene : alkane ratio in the reaction of CO₂ hydrogenation. Analogous effects are observed with a carbide catalyst synthesised by mechanochemical interaction of metallic iron with carbon.¹⁷² The authors do not discuss the nature of this phenomenon.

In virtually all the cases, changes in selectivity are related to the changes in the nature of the crystallographic facets upon grinding, while the influence of defects is not considered in any of the cited studies. In our opinion, it is necessary to take into account that the selectivity of multiroute reactions is determined by the ratio of several reactions, one of which yields the target product. Each reaction occurs on its own active centres, and by varying their ratio one can regulate selectivity. MCA can be a possible way of regulating the selectivity of catalysts. The increase in the selectivity of formation of target products is favoured by higher activity and a larger number of active centres responsible for the occurrence of major reactions and by a lower activity or a lower concentration of centres on which side reactions take place. By studying the dependence of the yield of various products on structural changes, one can establish the relationship between the occurrence of specific reactions and the presence of the corresponding structures, and this will contribute to the development of the theory of prediction of catalytic action.

Thus, the relevant, sufficiently numerous literature data point to a substantial influence of mechanical impact on the activities and selectivities of catalysts. Despite the long-standing opinion that it is impossible to use this effect for practical purposes because of the metastability of defects, some studies revealed high thermal stability of active states resulting from MCA and a substantial increase in the activities of catalysts of a number of industrially important low-temperature reactions. This is promising for the development of industrial technologies for increasing the activities of catalysts by MCA.

The reasons for the effect of MCA on the catalytic properties of compounds cannot nowadays be regarded as elucidated. The overwhelming majority of studies only state the facts of changes in catalytic properties resulting from mechanical impacts. The catalytically active centres are usually denoted with general terms, *viz.*, defects, distortions of the crystal lattice, *etc.*, without definition of their structures. Sometimes, changes in the activity (as a rule, its increase) are attributed to the appearance of specific defects: dislocations in the structure of various metals,^{105–112, 122} planes of crystallographic shear in the lattice of titanium dioxide,¹⁶⁵ steps on the facets {120} of Mn₂O₃,¹⁶⁰ dislocations with the known Burgers vectors in some oxides.¹⁶¹ We know only three studies^{122, 159, 165} which provided direct experimental evidence of the participation of defects of definite type in the increase in the

catalytic activity. The results of these studies allow description of the structure of active centres at the atomic level. In our view, the best successes in the investigation of the influence of defects on the activity of catalysts were achieved in the study of N_2O decomposition on copper oxide (the electronic theory of catalysis¹³² was used for its description) and in the investigation of the nature of the chemisorbed or surface oxygen involved in elementary catalytic acts.^{157–161, 164}

IV. The role of defects as active centres for chemical processes

Analysis of the literature data shows that compounds subjected to MCA exhibit increased reactivities in various chemical processes, *viz.*, simple chemical transformations, sorption processes and catalytic reactions. This indicates that defects are the active centres of all above-mentioned transformations. Let us consider a few examples of the versatile character of MCA action. Thus MCA of iron oxides increases both their catalytic activities in the CO oxidation and vapour conversion of $\text{CO}^{125–127}$ and the sorption capacity with respect to hydrogen sulfide.^{128, 129} Mechanochemical activation of vanadium(V) oxide induces symbatic modification of its sorption capacities with respect to sulfur dioxide and its activity in the SO_2 oxidation to SO_3 .¹²⁴ In addition, vanadium oxide manifests an increased activity in the reactions with hydrogen peroxide and alkalis after MCA.¹⁷³ Zinc and titanium oxides the structure of which contains shear defects, exhibit an increased activity in the CO oxidation^{162–165} and at the same time increased sorption capacities with respect to nickel and copper salts.^{97, 98} In addition, MCA increases the sorption capacity of zinc oxide with respect to hydrogen sulfide,³⁶ while titanium dioxide becomes more reactive in reactions involving oxygen¹⁶⁵ and sulfuric acid.³ The increase in reactivity is manifested also in a lower temperature of reduction, by hydrogen, of nickel chloride deposited on oxide supports subjected to MCA.^{97, 98} After activation of zinc ferrite with the structure of spinel, the rate of its dissolution in hydrochloric acid is substantially increased¹⁷⁴ together with the sorption capacity of zinc ferrite with respect to hydrogen sulfide.¹⁷⁵ In this state, zinc ferrite exhibits higher catalytic activity in the oxidation of CO.

Thus, if the sites of the exit of defects on the surface are catalytically active centres, they play simultaneously the role of sorption centres for salts from solutions and chemisorption of various gases, as well as of the reaction centres where simple chemical reactions take place. This refers not only to those defects which result from MCA but also to other defects. Thus the appearance of planes of twinning in the particles of metallic nickel in the formation of filamentous carbon leads to the increase in the specific rate of butadiene hydrogenation.¹⁷⁶ The reactivity of such nickel in the reaction with molecular bromine is also increased. As a result of interaction of silver supported on corundum with the reaction medium, one observes formation of interblock boundaries. These defects are the active centres of ethylene oxidation to ethylene oxide.¹⁷⁷ In the above-mentioned systems the character of oxygen chemisorption on silver and of hydrogen on nickel is changed.¹⁷⁸ Among uranium nitrides used as catalysts in the synthesis of ammonia, the maximum activity is characteristic of the sample with composition $\text{UN}_{1.7}$ with an ordered structure, *i.e.*, it has defects in the crystal structure of a definite type.¹⁷⁹ This nitride is also distinguished by a special character of chemisorption of nitrogen and a higher reactivity in the reaction with hydrogen.

These data show that the mechanically induced defects of the crystal structure exhibit higher activity in the three chemical processes differing in their nature and mechanisms: simple chemical transformations, sorption and catalysis (Table 3).

The increase in the sorption capacity of different oxides with respect to gases and the concomitant increase in their catalytic activities in the CO oxidation with formation of the same active centres is well explicable since chemisorption is an elementary

Table 3. Chemical processes depending on defects in the catalyst's structure.

Catalyst	Chemical transformation	Sorption	Catalytic reaction
ZnO	oxidation – reduction	O_2 , H_2Se , Ni^{2+}	oxidation of CO
TiO_2	oxidation, dissolution in acids	Ni^{2+}	the same
ZnAl_2O_4 , ZnFe_2O_4	leaching	Ni^{2+} , H_2S	"
Fe_2O_3	dissolution in acids	H_2S	"

stage of a catalytic reaction. But the fact that the increase in the activities of oxides in chemical reactions and stronger sorption of ions from solutions on them correlates with these two effects is surprising. Taking into account the versatility of active centres, one may suggest that the increase in chemical activity is explained not by changes in the mechanism of processes, but has a more common origin. It is changes in the thermodynamic potentials of compounds as a result of MCA that can be such a reason.

V. Catalytic reactions under conditions of mechanochemical activation

Scarce data on catalytic reactions occurring under MCA conditions may be divided into two groups: some of them are regarded as pseudocatalytic (the term proposed by P Yu Butyagin) and all other as really catalytic reactions. The so-called pseudocatalytic reactions represent a recurrent sequence of simple chemical transformations of reagents involving a solid. Each of these transformations may be regarded as an analogue of an elementary act in the stepwise mechanism of a catalytic reaction. Their motive forces are continuous induction of active centres as a result of mechanical impacts. For the reaction to continue after the interaction of reagents with the centre, the latter should be regenerated due to the supply of mechanical energy. In contrast to this, in the catalytic reactions the active centres are regenerated in subsequent elementary acts as a result of chemical transformations. Oxidation of carbon, hydrogen and CO under the conditions of mechanical activation of quartz^{180–182} represents examples of pseudocatalytic reactions. The mechanism of CO oxidation was described by Butyagin.⁵ Apparently reactions of polymerisation occurring upon mechanical activation of various materials in the medium of the corresponding monomers belong to the same type.^{183–185} Radical or charged centres of freshly formed surface act as initiators of the growth of polymeric chains.

The truly catalytic reactions include, *e.g.*, the synthesis of ammonia which takes place upon treatment of the catalyst with carborundum particles¹⁸⁶ in a jet mill¹⁸⁶ and in a ball mill,¹⁸⁷ hydrogenation of benzene on nickel in a vibratory mill,^{188–190} and of ethylene on iron,¹⁹⁰ and oxidation of SO_2 on vanadium(V) oxide.¹²⁴ All the above-listed reactions, except for the last mentioned one, proceed with high conversion degrees at room temperature. To accelerate the reactions of hydrogenation, solids possessing high hardness, *e.g.* corundum, were introduced into the reaction volume; these reactions can proceed even in the presence of catalytic poisons (thiophene).¹⁸⁸ The activation energy of sulfur dioxide oxidation in the temperature range 623–773 K under conditions of MCA was 5 kcal mol^{-1} , this energy being much lower than that in the conventional catalysis ($32–34 \text{ kcal mol}^{-1}$). Methanation of CO_2 on metal catalysts under mechanical activation is also carried out at elevated temperatures.¹⁹¹ Catalytic hydrogenation of CO to methane on the inert alloy $\text{Zr}_{0.5}\text{Ni}_{0.5}$ saturated with hydrogen is believed to follow two pathways.¹⁹² One of them includes the stage of dissociative chemisorption of CO with the liberation of elementary carbon and its subsequent hydrogenation; this is confirmed by studies of individual stages of the process under the MCA conditions. The

occurrence of the reaction through the second pathway is presumably associated with the generation of short-living active states on the catalyst surface.

We undertook systematic studies of catalytic reactions under the MCA conditions. This refers to many reactions: CO oxidation on oxides and metals, synthesis of ammonia on the industrial catalyst CA-1B, pyrolysis of butane on magnesium oxide, hydrogenolysis of butadiene on hydrides of magnesium intermetallides, synthesis of boric acid esters with the use of spherical granules of zeolites as catalysts, grinding bodies and absorbents of water formed in the reaction, as well as numerous reactions of hydrogenation and reduction of functional groups.^{163, 193} These reactions do not occur in the absence of catalysts, while the composition of the catalysts themselves is not changed in the course of the process. This indicates that they are indeed the accelerators of the process rather than mere reagents.

The reactions of hydrogenation and reduction of solid organic compounds have been studied in sufficient detail. The most efficient catalysts of such processes proved to be hydrides of intermetallic compounds. The mechanochemical reactions of catalytic hydrogenation or reduction involve only the terminal unsaturated bonds and functional groups; no reactions take place when these bonds and groups occupy internal positions. By varying conditions of mechanical activation, one can regulate the selectivity of reactions which has been clearly exemplified in transformations of caryophyllene α -oxide.¹⁶³ Apparently, in many cases, the mechanisms of reactions differ under the MCA conditions from those in traditional catalysis. Thus in the hydrogenation of butadiene under usual conditions on the hydride Mg_2FeH_6 the selectivity of formation of butenes is close to 100%,⁵⁶ whereas under the MCA conditions complete hydrogenolysis occurs on this catalyst.¹⁹³

How can MCA affect the course of catalytic reactions? One of the most important advantages of catalysis is the possibility of an easier overcoming the reaction activation barrier or, more precisely, its elementary act. This is as a rule achieved by supplying the catalyst and reagents with external energy, most often in the form of heat. The energy can also be supplied by sonication (sonocatalysis) or as electromagnetic radiation (radiation-induced catalysis or photocatalysis depending on the radiation wavelength).

We took the liberty of introducing a new term 'mechanochemical catalysis', *i.e.*, the catalysis in which the energy is supplied by mechanical impact on catalysts and reagents. As a result of such impact, not only the activities of catalysts are increased, but also the chemical reactivities of solid reagents and, besides, the regularities of activation of catalysts are changed. Since any measurements inside the working chambers of mills are not technically feasible, it may only be suggested what kind of processes occur during mechanical activation.

The simplest way is to suppose that the energy is supplied by means of transformation of the mechanical energy to thermal energy, after which a catalytic reaction occurs in a usual manner. Indeed, some investigators believe that the temperatures up to 1500–2000 K are developed at the sites of contact of grinding bodies with the compound under activation (the theory of magmaplasma). However, this view is not corroborated by valid experimental evidence. A conclusion based on calorimetric measurements which states that during grinding the temperature reaches 650–900 K seems to be better substantiated. Nonetheless, in this case, too, it is difficult to explain why at these temperatures either ammonium nitrate (published data) or some organic compounds (own results) virtually do not decompose. Apparently, introduction of compounds which can be readily activated changes the friction coefficients, while the temperatures in the working chambers are substantially lower under conditions of mechanochemical catalysis than those mentioned above. Hence, the transformation of the mechanical energy to thermal energy can explain only some of experimental data.

We believe that the most probable way of activation of reagents is the transfer of excess energy concentrated in the short-living centres formed in the course of cleavage of the catalyst's crystallites. Such centres have, as a rule, a radical nature, and the thermodynamic requirement for the reduction of their energy is fulfilled at the expense of bonding. The reactants situated in the immediate proximity of such a centre react with the unsaturated bond and pass to the activated state. In this case, the vibratory and electronic levels are excited, electronic levels appear in the forbidden bands (especially when defects of the crystal lattice are available), and the forbidden band becomes narrower. It is these processes that are the result of energy redistribution according to the scheme: mechanical energy $\rightarrow$ excess energy of the catalyst $\rightarrow$ excess energy of a reactant.

In contrast to other types of catalysis, the mechanochemical catalysis induces continuous formation of defects, their migration, interaction and annihilation. It is known that compounds are sorbed predominantly on sites of the exit of defects onto the surface and migrate together with these defects. Even dislocations of molecules into the bulk of solids were detected. Migration of point defects and dislocations is described in sufficient detail in the literature, but there is little information about the migration of planar defects. The planar defects are formed upon shear and turn the layers of cations and anions relative to each other. Apparently, recovery of the normal packing in some places and formation of shear defects in others occur in the MCA. In this situation, the places of exit of such defects migrate over the surface of crystallites. Interaction and annihilation of defects result in release of energy, and since the reactants are localised basically on defects, a part of the released energy is most probably spent in the activation of reactants.

We believe that the three modes of energy transfer mentioned above are the most probable since they are indirectly confirmed experimentally. One should not however rule out other ways of energy transfer to reactants. For example, the acceptor compounds may be activated by capturing the so-called mechanoelectrons. Several reports discuss the problem of participation of high-frequency phonons in the activation processes. Upon mechanical activation of solids, different types of electromagnetic radiation arise which can also induce activation of reactants in the mode similar to that of the radiation-induced catalysis or photocatalysis. Concomitant realisation of several described channels of energy redistribution is not precluded either.

VI. The nature of the effect of mechanochemical activation on the reactivity of solids

Using theoretical concepts, it is possible to predict to some extent, and in a number of cases to make approximate quantitative estimates of the effect of MCA on the properties of catalysts and catalytic reactions. Changes in the thermodynamic potentials of catalysts should induce changes in the equilibrium constants of formation of intermediate products, *e.g.*, chemisorbed compounds, towards their higher concentrations. With correct data on the values of thermodynamic potentials, it is possible to establish how changes in the catalyst's state influence its activity. To this end, use is made of the known expressions which relate the rate of a catalytic reaction to thermodynamic parameters. Such an approach is described, for example, by Boreskov.¹⁹⁴ At the qualitative level, one may say that the shift of equilibrium towards higher concentration of intermediates should lead to an increased reaction rate. It is obvious that both the magnitude of activity and its increment due to MCA have definite limits which are determined by the chemical nature of the compound subject to activation. The maximum of stored excess energy is determined by the type of crystal structure of a compound and by the nature of defects arising during MCA. In addition, if the appearance of defects results in changes in the heat of chemisorption of the

reactants, the activation energy of reaction (E) is also changed in conformity with the equation of Brønsted and Polanyi:

$$E = E_0 \pm \alpha q,$$

where the activation energy E_0 and the coefficient α depend on the type of reaction and q is the heat of chemisorption. This will also affect the rate of catalytic reactions. Upon formation of fresh surfaces by crystal splitting, localised free valences appear, the number of which may be close to the number of surface atoms. The presence of free valences favours the increase in the adsorption and chemical activities of the catalyst with respect to the gas and liquid phases and also solutes. Within the lifetime of such states, which ranges from 10^{-4} to 10^{-7} s (see Ref. 3), all processes of 'chemical relaxation' have enough time to occur, including chemical reactions with contacting compounds.⁴

The appearance of defects leads to changes in the electronic properties of a solid, which will be discussed below, and to changes in the geometry of the surface due to the appearance on it of sites for the exit of extended defects. Changes in the regular structure affect not only the sites of the exit of defects onto the surface themselves but also considerable areas around them. Relevant calculations indicate that at fairly moderate concentrations of dislocations (10^{11} – 10^{12} cm⁻²) the part of distorted structure amounts to 70%–80% of all the surface.³ For this reason, the defects of the crystal structure will substantially influence the processes of adsorption and hence the catalytic properties of a substance. This influence is realised through the geometric factor, *i.e.*, the geometric correspondence of the structure of reactants to the surface of catalysts. Apparently, the selectivity of multiroute reactions should vary most substantially. The sorption properties of the surface in the places of the exit of the defects of crystal structure should differ from those of the remaining surface, first, because of changes in the surface geometry and, second, due to the fact that such places serve as traps of electrons and possess special electronic properties.¹⁹⁵ The effect of defects on the catalytic properties of compounds is apparently also manifested in the variation of the energy of bonding between atoms in the lattice of catalysts which is determined by changes in the interatomic distances in the course of formation of extended defects. For example, the strength of the oxygen bond in oxides is well known to correlate with the catalytic activity of oxides in the reactions of oxidation. It is not excluded that the appearance of defects can result in changes in the nature of the chemisorbed reagents. Thus upon MCA of quartz the activated catalyst generates singlet oxygen; an analogous phenomenon is observed with the reduced and hence defective vanadium oxide.¹⁹⁶ This induces changes in the catalytic properties of this oxide in the oxidation reaction of naphthalene to phthalic anhydride.

Changes in the electronic properties of catalysts resulting from MCA can have a substantial effect on the redox and other reactions requiring transfer of electrons. We have already noted above that chemisorption is possibly influenced by changes in the surface properties in the places of the exit of defects where electrons are localised. It may also be expected that during the occurrence of both catalytic and ordinary reactions the conductivity electrons and the electrons belonging to anions with enhanced electron-donor properties will be involved in the elementary acts with electron transfer. According to the literature data, the catalytic properties of compounds can be influenced by the peculiarities of transition of electrons from one electronic level to another, work of electron release, position of the Fermi level, width of the forbidden band, availability of electronic levels in it, *etc.* All these parameters may be influenced by means of MCA.

All the changes listed above favour the increase in the reactivities of components in the synthesis of catalysts, modification of their sorption properties due to the formation of new surface and the appearance of places for the exit of defects onto the surface, as well as changes in the specific catalytic activity. By now, a considerable body of experimental data has been accumulated on the dependence of the catalytic activity on the mechanical impact.

However, the authors of the overwhelming majority of works confine themselves either to a trivial statement of such influence or to attempts to explain specific situations that they have observed.

Comparison of different viewpoints would possibly allow interpretation of experimental observations, formulation of general theoretical concepts and creation of the scientific ground for the purposeful control of the processes occurring. Of special interest is the elucidation of the reasons of the effect of MCA on the catalytic activity of compounds and selectivity of reactions of different nature (redox, acidic and other reactions). To this end, physical theory of mechanical impact should be combined with concepts of the chemical nature of the catalytic activity. It is possible that this will not however allow creation of an integral theory, as it is still the case in the heterogeneous catalysis on the whole, but there is a possibility to formulate local theoretical conceptions relevant to individual types of catalysis.

The problem of estimation of the specific activity of a catalyst is of crucial importance. The well known Boreskov's rule on the approximately constant specific activities of catalysts of the same chemical compositions¹⁹⁴ may be regarded only as a statement of the chemical nature of a catalytic act which was formulated by Berthelot as far back as 1877: 'Owing to a chemical impact of contacting substances, intermediate compounds are formed which in turn are degraded as they emerge and eventually vanish in the final metamorphosis.'¹⁹⁷ If the catalytic properties of compounds were determined solely by the chemical composition of active centres, then it would be absurd to expect that the same centres could display different activities, and no additional experiments would have been required.

The constancy of specific catalytic activity is approximate in the extent to which the total set of properties of the surface of catalysts is reproduced. The actual level of the development of the scientific bases underlying the preparation of catalysts does not allow high reproducibility. However, from the viewpoint of applied science this is not required in most cases. The term 'approximate constancy' means that the activity of catalysts is also influenced by other factors which were not denied by Boreskov either (see his monograph,¹⁹⁴ p. 47). In his opinion, these factors can induce differences in properties of individual facets of crystals and the non-equilibrium states of the catalyst's surface. But even the catalysts with completely the same chemical, structural and other characteristics would possess an approximate rather than absolute constancy of specific activity.

It is the role of additional factors which influences the specific catalytic activity that was the topic of our review. The activity of a catalyst with defects is somewhat higher than its activity in the equilibrium state. The degree of increase in activity depends on the amount of excess energy which is stored in defects and influences the catalytic properties through the variation of thermodynamic potentials. This amount of energy is determined by the physico-chemical nature of the catalytically active sites.

The non-equilibrium structural and phase states of catalysts arising in the process of their preparation should be subject to annealing in the course of reaction, and the catalysts should pass to the steady state. However, there are numerous examples of rather high stability of such states of solid catalysts at elevated temperatures in real reaction media. This is explained by the fact that thermal annealing of defects is an activation process, and if the conditions do not permit overcoming of the activation barrier, some metastable structures of higher reactivity may exist for a rather long time.

Further studies of the nature of the structural factors and of their role in a chemical act will allow a deeper insight into the detailed mechanism of catalysis. The progress in this field can be achieved using novel MCA techniques and modern physical methods of research.

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^g — *Crystallogr. Rep. (Engl. Transl.)*

Biodegradable starch-based polymeric materials

A I Suvorova, I S Tyukova, E I Trufanova

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Abstract. The effects of low-molecular-weight additives, temperature and mechanical action on the structure and properties of starch are discussed. Special attention is given to mixtures of starch with synthetic polymers, *e.g.*, co-polymers of ethylene with vinyl acetate, vinyl alcohol, acrylic acid, cellulose derivatives and other natural polymers. These mixtures can be used in the development of novel environmentally safe materials (films, coatings, packaging materials) and various articles for short-term use. The bibliography includes 105 references.

I. Introduction

Modern-day technology calls for the development of polymeric materials the properties of which do not change even after long-term use. The effects of environmental factors (*e.g.*, water, atmospheric oxygen, sunlight and biological agents, such as microbes, fungi, insects, *etc.*) reduce the service life of many articles prepared from polymeric materials. All this raises the problem of creation and application of special-purpose stabilisers and bioprotectors.¹ However, the immense bulk of polymeric materials and articles made thereof puts forward a problem of their further destruction or disposal after the termination of their service life. Many polymers are decomposed in the environment over a relatively long period of time; therefore, the production of biodegradable materials is as important as their stabilisation. Polymers, particularly household plastics and films, must be rapidly decomposed after use under the influence of chemical (atmospheric oxygen, water), physical (sunlight, heat) and biological (bacteria, fungi, yeasts, insects, *etc.*) environmental factors.^{2,3} These factors produce a synergistic effect, eventually resulting in the fragmentation of the polymer owing to the destruction of its macromolecules and their conversion into low-molecular-weight compounds that can be further involved in the natural circulation of substances. In the strict sense, the term 'biodegradation of a polymer' implies deterioration of its physical and chemical properties and a decrease of its molecular mass

down to the formation of CO₂, H₂O, CH₄ and other low-molecular-weight products under the influence of microorganisms in both aerobic and anaerobic conditions.^{4,5}

Microorganisms or enzymes produced by them cause the decomposition of natural polymers (*e.g.*, cellulose, starch, chitin, polypeptides, *etc.*) into low-molecular-weight compounds which are further involved in the metabolism of the elemental forms of life.⁶ Enzymes play the role of catalysts favouring the degradation of the main polymeric chain. Specific enzymes evolved in the course of evolution can selectively destroy natural high-molecular-weight compounds, such as cellulose, proteins and other natural polymers. For example, amylase induces the degradation of the starch molecule. Enzymes causing the destruction of synthetic polymers, *e.g.*, polyalkenes or polyvinyl polymers, are absent in Nature. However, these classes of polymers are especially extensively used in the production of packaging materials and articles for short-term use. These wastes constitute the greater part of municipal garbage in all industrially developed countries.^{2,7–9} The interest in materials based on natural polymers (*e.g.*, starch, chitin) has increased considerably in the recent years, because owing to their structural features these compounds can be involved in natural circulation and thus be environmentally safe.

The problem of development of biodegradable polymeric materials has been considered in detail in reviews.^{10–13} It was shown that the use of natural renewable polymers is the most promising and economically advantageous approach. The synthesis of novel biodegradable polymers and chemical modification of natural polymers were described by Vasnev.¹⁴ The methods for estimating the biodegradability of polymeric materials based mainly on the analysis of products of the activity of bacteria which decompose polymers have been developed and standardised in many countries.^{4,15–17}

Here we survey the most recent data concerning the properties of materials prepared from starch or its mixtures with synthetic polymers.

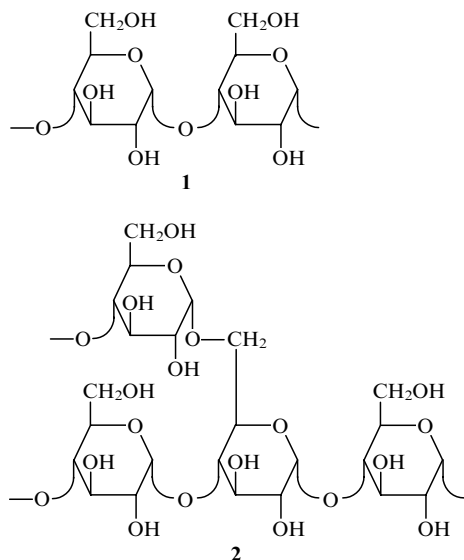
II. The structure of starch

Starch is a natural polysaccharide which is accumulated in plant tubers, seeds, stalks and leaves in the course of their vital activity. The main sources for the commercial production of starch are potatoes, wheat, corn and rice. Starch comprises two polymeric components, *viz.*, amylose and amylopectin, they are built of α -D-glucopyranose residues but differ in both structure and function. The amylose content in native starch usually varies from 20 mass % to 30 mass %, while amylopectin constitutes the greater part (70%) of the starch molecule. At the same time, the

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amylose content in high-amylose starch can reach 50 mass % to 70 mass %.¹⁸

Amylose (**1**) is a linear polymer, which consists of α -(1,4)-D-glucopyranoside residues with the average molecular mass of $\sim 10^2$ to 10^3 kg mol⁻¹. In cellular starch, the helical chains of amylose form complexes with lipids. Amylopectin (**2**) contains α -(1,4)- and α -(1,6)-linked glucose residues. Extended linear chains involve α -(1,4)-bonds and a great number of shorter branchings are linked through α -(1,6)-bonds.



The molecular mass of amylopectin is approximately 10^5 kg mol⁻¹. The branchings in the starch molecule may contain, on the average, up to twenty glucose residues. Amylopectin molecules also form helices; it is noteworthy that shorter side chains form double helices.^{19,20}

The spatial structure of amylopectin has not been clearly understood yet. A number of models have been proposed²¹ in order to establish a correlation between the character of branchings in the chains of amylopectin and its ability to form regular crystalline regions. The Robin–Mercier scheme²² (Fig. 1) pro-

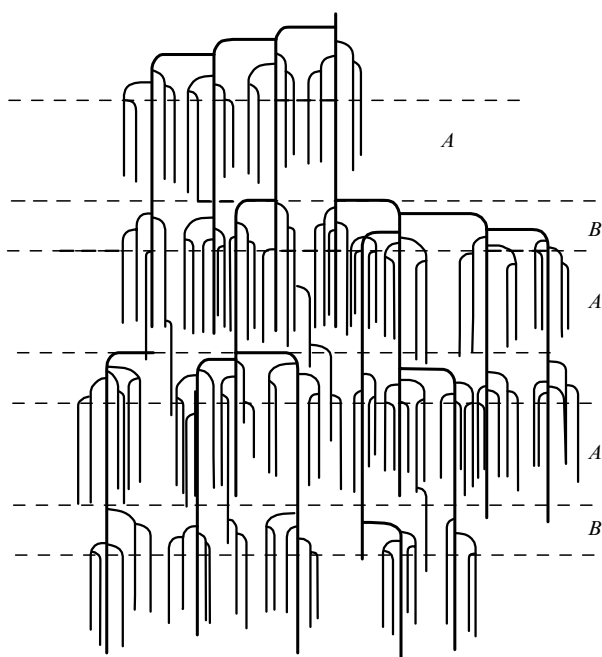


Figure 1. A structural model of amylopectin; A are crystalline regions, B are amorphous regions.²²

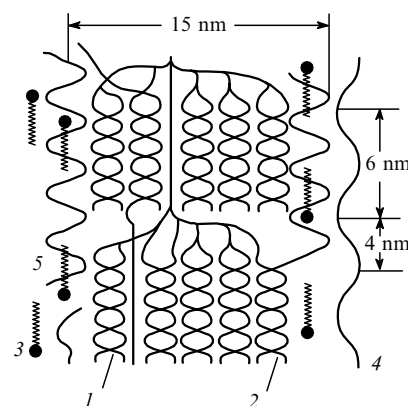


Figure 2. The structure of native starch;²⁰ (1) helices of amylopectin, (2) hybrid helices of amylose and amylopectin, (3) free lipids, (4) free amylose, (5) V-structures of amylose.

vides an example of such models. This model takes account of the presence of amorphous regions in the amylopectin molecule formed by chain branchings and of crystalline regions consisting of linear, parallelly stacked fragments.

The degree of crystallinity of natural starch depends on its origin and varies from 15% to 45%. The structure of starch formed by regular stacking of the double chains of amylose and amylopectin and incorporating lipid molecules which form complexes with them is schematically represented in Fig. 2. Using wide-angle X-ray scattering,^{19,23} it was shown that the crystalline structures of starch isolated from different parts of plants differ considerably. This polysaccharide was found to exist in three polymorphous modifications. Starch from gramineous seeds has the so-called A-structure, tuber starch has the B-structure, while starch extracted from roots and stalks of plants has the C-structure. The crystalline structures of the A- and B-types are associated with the amylose fragment and consist of parallel coiled right double helices with anti-parallel packing. Each turn of the helix comprises six α -D-glucose residues. The conformations of the double helices of amylose in A- and B-structures are identical, but the A-structure is represented by a unit cell of the orthorhombic type ($a = 1.190$ nm, $b = 1.770$ nm, $c = 1.052$ nm), whereas the B-structure is represented by a hexagonal unit cell ($a = b = 1.85$ nm, $c = 1.04$ nm). Besides, in natural starch amylose complexes with lipids form structures of the V-type. The content of crystalline structures of the A- and B-type in starch samples of different origin was found to be 56% and 44%, respectively.²⁴ The presence of these structures was confirmed by IR spectroscopy.²⁵

Starch contains a large proportion of amorphous regions. However, the glass-transition temperature (T_g) of dry starch cannot be measured because it lies above the temperature at which the decomposition of the polymer occurs; its calculation is based on the estimation of the plasticising effect of water which penetrates into the amorphous regions of the starch molecule and decreases T_g . The concentration dependence of T_g of the starch – water system can be described by the equation²⁶

$$T_c = 244.9 - 1565\omega + 2640\omega^2,$$

where ω is the content of water (w/w) in swollen starch. Extrapolation of these data for T_g of the starch samples plasticised with water to various degrees gave T_g values ranging from 230 to 250 °C.^{20,26}

Starch is present in plants in the form of granules having the diameter from 2 to 100 μ m.²⁷ The structure of these supramolecular granules is complex and has not yet been finally elucidated. It is known that starch granules comprise both crystalline and amorphous regions. The amorphous regions form a continuous phase and incorporate crystals of a lamellar type.²⁷ Microscopic analysis of the supramolecular structure of starch granules²⁸

revealed that the lamellae predominantly consist of amylopectin. Their sizes depend on the origin of starch and their localisation in the granules and vary from 20 to 500 nm.

Starches isolated from different natural sources differ in their sensitivities to destructive factors, such as temperature and enzymic hydrolysis. Thermolysis of starch granules isolated from potatoes, wheat, barley, rice, corn and tapioca was studied at fixed temperatures (170–325 °C).²⁹ It was found that corn starch exhibits the highest resistance to heating, whereas barley starch is the least thermostable. This may be due to the differences in the molecular masses and ratios of linear and branched components of starches having different biological origin.

III. Effects of water and plasticisers on the properties of starch

Starch is a typical hydrophilic polymer; it may contain up to 30 mass %–40 mass % of bound water. It is known²³ that different structures of starches of the A- and B-types bind differently to water. In structures of the B-type, water is mobile and can easily enter and leave the complex (Fig. 3). In crystallites of the A-type, water of hydration forms a layered structure and is firmly bound to the surrounding double helices of amylose. Therefore, A-structures are less sensitive to the atmospheric moisture than B-structures.

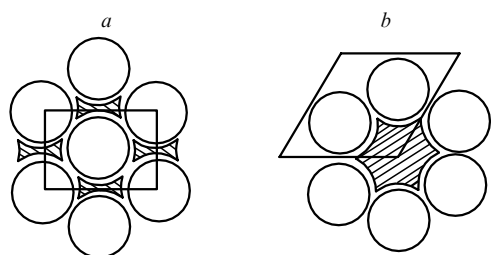


Figure 3. The schematic representations of the crystalline structures of amylose with water. (a) A-amylose complex, (b) B-amylose complex. The hatched areas designate absorbed water.

Studies of the effect of water on starch provide additional information about the structure of this polymer. Dissolution of starch in water is a complex process, which strongly depends on temperature. Swelling of starch in saturated water vapour at room temperature results in the formation of a gel which retains the predominant polymer-to-polymer contacts.³⁰ This process does not result in complete dissolution of starch as is evidenced by the shape of the isotherm of water vapour sorption³¹ characteristic of systems with limited swelling of a polymer. However, the mobility of starch molecules increases with an increase in the amount of absorbed water as a result of which the linear component of the polymer, *viz.*, amylose, forms a true solution with water. This is accompanied by the formation of a two-phase swollen gel–solution system.

A high-energy interaction with water of several samples of amylose starch having a crystalline structure of the B-type and the chain length of 12–55 residues was established by scanning calorimetry and sorption.³² However, at room temperature the energy of the interaction of the components is too low to compensate for the oppositely directed entropic contribution. Therefore, complete destruction of the polymer-to-polymer contacts and solubilisation of starch do not occur. Water is a poor solvent for amylose starch at room temperature.

The solubility of starch increases with temperature. The swelling of dispersions (2.6 mass %) of corn and pea starches in water was studied by laser diffractometry.³³ It was found that heating above gelatinisation temperatures significantly changes both the sizes of starch granules and their distribution according

to size. The maximum increase in the diameter of starch granules is ~ 3.5-fold.³³ The behaviour of the starch–water system at a wide range of temperatures was studied by differential scanning calorimetry (DSC), dilatometry, rheology and polarisation microscopy using rice,³⁴ potato^{26,35} and wheat³⁵ starches as examples. The sizes of starch granules first increase slightly in excess of water at 35 to 55 °C and then increase sharply (by 55%) at 65 °C, reaching the maximum at 75 °C. At temperatures above 75 °C, starch granules are destroyed and crystallinity disappears. The viscosity of the system kept at the temperatures indicated above increases until the gelatinisation step is reached. At higher temperatures, amylose is separated from amylopectin due to partial destruction of the physical lattice nodes after which starch dissolution begins. Cooling of aqueous solutions of starch again results in the formation of gels which contain swollen granules consisting predominantly of amylopectin; the amylose component of starch is predominantly localised in the intergranular space.

The dissolution of rice starch was studied by DSC and was interpreted³⁴ as a phase transition, since the thermograms displayed a peak of heat absorption at 75 °C corresponding to the gel transition. Using DSC, it was shown that the increase in the water content in wheat starch from 2.8 mass % to 90 mass % and subsequent heating induced several structural transitions due to melting of amylopectin crystallites and its complexes with lipids as well as due to melting of amylose in the swollen samples.³⁶

The content of amylose and amylopectin, their molecular masses and the content of lipids depend on the origin of starch. These factors affect the interaction of starch with water. The gel-forming abilities of starches isolated from the grains of hard and soft corn,³⁷ hard wheat and potatoes grown in different geographical zones, from rice³⁴ and green herbs³⁸ have been studied. It was shown that starches isolated from gramineous plant seeds contain less amylose than potato starch and have lower values of the temperature and enthalpy of gelatinisation. In contrast, starches isolated from green herbs, which contain more amylose (up to 30 mass %) of high molecular mass (up to 4.5×10^3 kg mol⁻¹) and highly branched amylopectin, have higher values of these parameters.

Studies on the structure and gelatinisation of amylopectin samples ($M_w = 0.2 \times 10^3 - 1 \times 10^3$ kg mol⁻¹) specially prepared from yellow corn revealed²¹ that the gels kept at constant temperature (4 °C) are typical representatives of thermoreversible gels formed by physical lattice nodes. The crystallinity of such gels increases upon storage as can be evidenced from wide-angle X-ray scattering data²¹ and the increase in the area of the endothermal peak on the DSC curves^{21,39} resulting from the increase in the enthalpies of melting of starch crystallites. Apparently, water which plays the role of a plasticiser by increasing the mobility of starch granules increases the crystallinity as in the case of the synthetic polymers.⁴⁰ It was also shown²¹ that the structural perfection of amylopectin crystallites depends on the conditions of gel crystallisation.

The interaction of starch samples differing in the amylose content with water was studied by Shogren and Jasberg.¹⁸ The behaviour of corn starch containing 28 mass % of amylose in the swelling and subsequent gelatinisation differs considerably from the behaviour of starch with the amylose content of 50 mass % to 70 mass % at equal molecular masses of the polymers. These differences affect starch concentrations at which gelatinisation begins, enthalpies of gelatinisation and the syneresis rates of the gels.

The effect of the molecular mass of the amylose starch on its solubility was studied by Moates *et al.*³² With a change in the molecular masses from 2 to 10 kg mol⁻¹ in systems with the same degree of swelling (0.8), the dissolution temperature of starch increases from 57 to 119 °C. Extrapolation to infinitely high molecular mass gives a dissolution temperature of 147 °C.

It was found^{41,42} that homogenisation of wheat or potato starch in water is facilitated by mechanical action on the system, *e.g.*, by extrusional stirring of the components. It was shown⁴²

that the threshold of a twin-screw extruder of the mixer driver is 120–150 kW h⁻¹ below which the system cannot pass into the fluid state. This limiting value depends on the viscosity of the mixture, which is proportional to the molecular masses of amylose and amylopectin.

Plasticisation of starch with water and its simultaneous exposure at elevated temperature and under mechanical stress makes it possible to change considerably the physical and mechanical properties of the starch–water system. The reason for these changes is in irreversible destruction of starch granules, mechanical stress being the crucial factor in this process. Reprocessing of plasticised starch on standard technological equipment for moulding of plastic materials (*e.g.*, extruders, casting machines, *etc.*) permits one to obtain materials possessing different physical properties.

Glycerol and oligomeric polyglycols can also exert a plasticising effect on starch. These plasticisers are generally used in combination with water. The thermoplastic properties of materials obtained by extrusion of mixtures of potato starch with glycerol and water were studied by van Soest *et al.*⁴³ Two specimens were studied based on the native starch, *viz.*, that with $M_w = 37\,000\text{ kg mol}^{-1}$ and that with $M_w = 1900\text{ kg mol}^{-1}$ prepared by partial acid hydrolysis. The specimens containing less than 9 mass % of water were glass-like and had elasticity moduli from 400 to 1000 MPa. If the water content in these materials was from 9 mass % to 15 mass %, they acquired elastic properties but became soft and fragile with an increase in the water content above 15 mass %. The differences in the thermoplastic properties of these materials are due to the presence of water rather than to the differences in the molecular weights of the starches. Thermo-mechanical analysis revealed that T_g of the extruded samples decreased appreciably with an increase in the water content (Table 1). It was assumed^{43,44} that the properties of starch-based thermoplastic materials are determined by the formation of a complex network consisting of linear chains of amylose and branched molecules of amylopectin in which hydrogen bonds play a crucial role. A lower value of the fracture energy of an elastic material prepared from low-molecular-weight starch can be attributed both to the shorter length of the amylose chain and to smaller molecular mass and branching of the amylopectin molecules.

Table 1. The changes in T_g of extruded samples of potato starch plasticised with water.⁴³

Water content (mass %)	T_g / °C	
	material prepared from native starch	material prepared from hydrolysed starch
14	5	—
11	25	—
8	42	—
5	59	58

The effects of glycerol (14 mass %–39 mass %) and water (1 mass %–28 mass %) on the phase behaviour of barley starch were studied using DSC and dynamic thermomechanical analysis.⁴⁵ Samples with low content of water and glycerol formed homogenous monophasic systems. Strong interaction of starch with glycerol in samples containing less than 20% of water presumably impedes crystallisation of amylopectin as a result of which the system remains amorphous and monophasic. With an increase in the concentration of the plasticising agents, the mixture separates into a starch-enriched and a starch-depleted phases as evidenced from the appearance of mechanical loss peaks corresponding to T_g of the individual phases.

Simultaneous use of water and glycerol as plasticisers makes it possible to obtain flexible starch-based thermoplastic materials by

compression moulding⁴⁶ and extrusion.⁴⁷ The materials prepared from corn, potato and wheat starches were characterised by constant (with respect to starch) content of glycerol (1:0.3), contained from 8 mass % to 25 mass % of water and were elastic ($T_g < 20\text{ °C}$). Studies of mechanical properties of such materials established a dependence of the elasticity modulus and breaking stress (σ_p) both on the content of the plasticising agents and on the origin of starch.^{46,47} The difference in mechanical properties is presumably due to the higher content of amylopectin in corn starch, which is plasticised with water more readily than potato starch enriched with high-molecular-weight amylose.⁴⁷

The mechanical properties of plasticised starch depend on the storage time prior to testing.^{48,49} Storage of thermoplastic materials prepared from corn⁴⁸ and potato⁴⁹ starch at high relative humidity (up to 90%) results in an increase in their breaking stress, while their elongation at disruption decreases. The reason for this phenomenon is the time-dependent post-crystallisation of starch in the presence of water and glycerol; the degree of crystallinity of B-type structures in the tested samples increases from 5% to 30%.

The amylose and amylopectin components of starch plasticised with water and glycerol manifest different abilities for structural rearrangements.⁵⁰ Analysis of extrusion samples of specially prepared high-amylose and high-amylopectin starches (the amylose content varied from 0% to 70%) revealed⁵⁰ that in amylose-enriched materials further crystallisation occurs much faster than in amylopectin-enriched ones.

The higher ability of plasticised amylose for post-crystallisation was also established in samples of the amylose starch obtained by compression moulding.⁵¹ The elasticity moduli of plasticised, partially crystallised samples comprising structures of the V- and B-types were practically the same immediately after moulding. After storage, the elasticity moduli of the samples prepared from normal corn starch was ~100 MPa, whereas those of the high-amylose starch were of about 700 MPa. These differences seem to be due to the fact that high-amylose starches contain more amorphous structures capable of additional crystallisation.⁵¹

Storage of samples also causes certain changes in T_g due to the condensation of amorphous regions of starch as a result of formation of additional nodes on the physical lattice and conformational rearrangement of the macromolecules, leading to the formation of molecular and intramolecular double helices of amylose and amylopectin.³⁹

In addition to glycerol and polyglycols, other substances can exert a plasticising effects on starch. Calorimetric determination of T_g of starch films containing water and additives (10%–20%) of glycerol, sorbitol, sodium lactate, urea, ethyleneglycol, diethyleneglycol, polyethyleneglycol (PEG-200) and glycerol diacetate was carried out by Lourdin *et al.*⁵² All these compounds, with the exception of glycerol diacetate, formed homogeneous systems with starch; their T_g decreased monotonically with an increase in the concentration of the plasticisers. The glycerol acetate–starch system was characterised by phase separation; the value of T_g did not change in the presence of the plasticiser.

The water in the starch not only transfers the system into a thermoplastic state upon extrusion, but also partly protects the polymer from destruction. For example, sage starch which contained from 34% to 47% of water was incapable of dextrinisation (*i.e.*, degradation leading to low-molecular-weight and oligomeric carbohydrates) but was easily gelatinised, if the extrusion was carried out under drastic conditions (150 °C, high screw speeds).⁵³ According to other investigators, the processing of this polysaccharide into a thermoplastic material is always accompanied by destruction. Thus, mixing of yellow corn starch⁵⁴ with water (18 mass % or 23 mass %) in a two-screw extruder decreases its molecular mass from 3.36×10^5 to $4 \times 10^4\text{ kg mol}^{-1}$. After repeated extrusion in a single-screw extruder at 110 or 130 °C, the decrease in the molecular mass is less pronounced. It was proposed⁵⁴ to use the value of specific mechanical energy applied to the polymer on moulding for the calculation of the expected

decrease in the molecular mass when choosing the type of the extruder and the regime of moulding of thermoplastic materials.

Water and other agents containing hydroxy groups are used as additives in the preparation of thermoplastic materials for single or short-term use. A significant drawback of these materials is their low resistance to water. Therefore, in recent years starch mixtures with synthetic polymers have acquired increasing importance together with thermoplastic materials prepared from starch without additives. These materials combine characteristic properties of their synthetic component with biodegradability owing to the presence of a natural biodegradable component, *viz.*, starch.

IV. Mixtures of starch with synthetic polymers

Composite starch mixtures with various synthetic polymers were first proposed in the 1970–1980's.^{55–59} Most often, starch is used for the modification of polyethylene (PE), a film material designed for short-term use (*e.g.*, packaging of food stuffs, agriculture and medicine, *etc.*). In these mixtures, starch usually plays the role of a filling agent, which ensures the biodegradation of the polymeric item after its service life is over.⁶⁰ Thermoplastic mixtures of synthetic polymers with starch are typically prepared from starch plasticised with glycerol and water. The components are mixed in an extruder at $\sim 150^\circ\text{C}$, which temperature ensures good gelatinisation of the polysaccharide⁶¹ and leads to the formation of two-phase mixtures the biodegradation of which begins from the surface of a starch-enriched film. Small amounts of pro-oxidants favour biodegradation by inducing oxidative decomposition of the material under natural conditions.⁶² A PE–starch–vegetable oil mixture is an example of such a composition.⁶³ Vegetable oil plays the role of a pro-oxidant and simultaneously facilitates the mixing of the natural and synthetic polymers in the course of moulding.

Starch is poorly compatible with non-polar PE; therefore, investigations into improvement of the affinity of the natural and synthetic polymers should be aimed at preparing starch mixtures with co-polymers of ethylene with other more polar monomers as well as at producing modified starches with enhanced affinity for PE.

1. Mixtures of starch with ethylene co-polymers

Co-polymers of ethylene with vinyl acetate (EVAc) or the products of saponification of acetate groups in these co-polymers are most commonly used as components of starch mixtures. These mixtures are prepared from yellow or native corn as well as from high-amylose starch Hylon VII by extrusion with the ethylene–vinyl alcohol co-polymer [EVAL, 56% of $\text{CH}_2\text{CH}(\text{OH})$ units]. Their structural characteristics were studied by wide-angle X-ray scattering, scanning and transmission electron microscopy and DSC.⁶⁴ Heterogeneous mixtures of EVAL with yellow corn starch displayed a clearly defined boundary between the phases; the sizes of the domains were proportional to the extrusion time. In heterogeneous mixtures of EVAL with native corn and Hylon starches, the inhomogeneities decreased faster than in the case of yellow corn starch; the boundaries between the phases as seen in the electron micrographs were diffuse. There was a decrease in the melting temperature of the synthetic polymer, which testified to partial miscibility of the components at the interphases. Simmons and Thomas⁶⁵ prepared phase-separated mixtures of various compositions, which contained domains (0.1–3 μm) enriched either with starch or with EVAL depending on the composition. At the starch content of 55 mass %–60 mass %, the phase reversal was accompanied by drastic changes in the domain sizes. An analysis of the phase compositions of starch mixtures revealed that the compatibility of the components increased with an increase in the amylose content in the starch.

Fibres cast from these mixtures manifested reduced sensitivity to moisture and low initial rates of enzymic biodegradation even in starch-enriched systems. The surface of these fibres was coated with a layer of a synthetic co-polymer, since the matrix phase of

the system was EVAL with the starch content of up to 70 mass %.^{64,65}

The water resistance and mechanical properties of starch mixtures are determined by the ratio of their constituents. Absorption of moisture by films⁶⁶ prepared by blowing of mixtures of native corn starch pre-plasticised with glycerol and water and EVAL [1:1 (mixture A); 2:1 (mixture B)] varied from 2% to 11% and was greater in the films prepared from mixture B. The breaking strength of the films prepared from mixture A was one-third of that for films prepared from pure EVAL and even less for films prepared from mixture B.

The use of electron irradiation (flux energy 2.5 MeV, 2500 Gray s^{-1}) in the formation of thermoplastic EVAL–starch mixtures makes it possible to modify the structure and rheological properties of these compositions.^{67,68} EVAL was shown to be resistant to irradiation, which causes predominantly destruction of starch macromolecules by changing their supramolecular organisation and thus facilitating the mixing of starch with EVAL. The mechanical and rheological properties of irradiated mixtures differ substantially from those of the original samples. The mixtures containing high-amylose starch appeared to be the most resistant to irradiation, which can be attributed⁶⁸ to chemical reactions of the linear molecules of the amylose starch with the synthetic polymer under the influence of irradiation.

The conditions for moulding of starch mixtures with EVAL strongly influence their degradability. The favourable effect of the structural anisotropy of starch–EVAL mixtures which appears in the injection moulding on the resistance of the mixtures to the action of physiological solutions (estimated from the mass loss and changes in the mechanical properties upon ageing for 80 days) and ethylene oxide used for the sterilisation of materials in clinical practice was demonstrated by Reis *et al.*⁶⁹

In-depth studies into the properties of starch mixtures with EVAc and with EVAc modified with maleic anhydride (EVAMA) were carried out by Ramkumar *et al.*^{70–74} Mixtures of commercial corn starch (25 mass % of amylose, 75 mass % of amylopectin) with co-polymers containing 18 mass % (EVAMA-18) and 28 mass % (EVAMA-28) of CH_2CHOAc units and about 0.8 mass % of anhydride fragments were prepared by extrusion carried out at different temperatures, screw speeds and mixing times. A dynamic mechanical analysis⁷² performed at different shear rates (0.005–0.5 s^{-1}) and frequencies (0.1–100 s^{-1}) in a broad range of temperatures revealed that all the mixtures under study displayed two regions of relaxation transition temperatures, *i.e.*, -30°C for the synthetic polymer and 40°C for starch, which testifies that these systems are heterogeneous. The introduction of anhydride fragments into the co-polymer macromolecule causes a shift in the transition temperatures, which suggests improved compatibility of the components.

The changes in the crystallinity of starch granules in the course of mixing were demonstrated by DSC.⁷² The starch–EVAMA mixtures are characterised by lower values of heats of melting (Table 2), *i.e.*, the structure of starch granules in these mixtures changes to a greater degree. Repeated compression moulding of the mixtures also decreases the heat of melting.

With an increase in the starch content in the mixtures, the viscosity of the systems changes, reaching a maximum level at 70 mass % of starch. The absolute viscosities of the mixtures containing EVAMA-18 are higher than those of starch–EVAMA-28 mixtures. It is noteworthy that the viscosities of starch mixtures of any composition exceed the additive values.^{72,73}

The ability of starch mixtures to absorb water strongly depends on the moulding conditions, *e.g.*, temperature, screw speed and injection pressure. Starch–EVAMA mixtures absorb water more readily than starch–EVAc mixtures (22 mass %–37 mass % or 20 mass %–27 mass % of water, respectively). Contrariwise, in the presence of water the values of diffusion coefficients and structural relaxation times calculated from the anomalous sorption model were higher for starch–EVA mixtures. These differences were attributed to the different degree of

Table 2. The heats of melting of starch mixtures with ethylene co-polymers.⁷⁰

Sample	Heats of melting ^a of samples /J g ⁻¹	
	following extrusion	following additional compression moulding
Starch–EVA ^b		
20:80	—	75.8
40:60	101.0	95.5
Starch–EVAMA-18 ^b		
40:60	46.9	19.7
70:30	—	98.0
Starch–EVAMA-28 ^b		
40:60	56.6	26.0
70:30	—	68.7

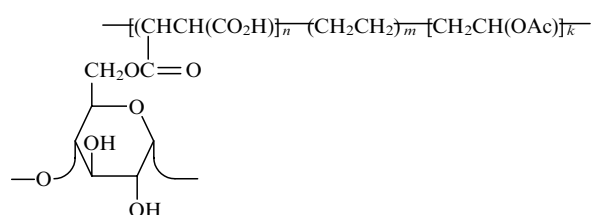
^aThe heat of melting of dry starch is 35.9 J g⁻¹; ^bThe figures in parentheses designate the starch:co-polymer ratios.

starch destruction during the formation of mixtures with EVAc and EVAMA rather than to the presence of anhydride groups in the co-polymer.⁷⁰

Using wide-angle X-ray scattering, it was shown⁷³ that 20-week storage of starch mixtures with a synthetic polymer leads to structural rearrangements resulting in the restoration of the crystalline structure of starch, which was completely lost in the course of moulding. The changes in crystallinity are especially well-pronounced during the first five weeks following moulding; as a result, the resistance of starch samples to rupture increases. After storage of the samples at 10 °C, the structural changes become less apparent, but are manifested on storage at 50 °C, since relaxation transitions in starch occur around this temperature.⁷²

From the data taken altogether, Ramkumar *et al.*^{70–74} concluded that the presence of anhydride fragments in the co-polymer chain is favourable for the improvement of compatibility of the starch mixture constituents. Mixtures of co-polymers of EVAc and EVAMA with the starch content of 70 mass % manifest good mechanical and moulding properties and are fairly resistant to water.

Mixtures of starch with an ethylene–propylene co-polymer (EP), polystyrene (PS), an ethylene–propylene–maleic anhydride co-polymer (0.8 mass %, EPMA) as well as with a styrene–maleic anhydride co-polymer (8 mass %, SMA) obtained by extrusion at 120–180 °C were studied at different effective mechanical moulding energies.^{75–79} In these studies, the effects of the composition (40 mass %–70 mass % of starch) and moulding conditions on the structure and properties of starch mixtures were analysed. As in the case of starch–EVAMA mixtures,^{70,72} the miscibility of components improved in the presence of anhydride fragments in the synthetic polymer chain. This phenomenon was interpreted^{75–79} as the chemical reaction between starch and the synthetic polymer under the influence of high temperatures and shear stress in the extruder on moulding. This reaction results in the formation of ester bonds between the carboxy groups in the co-polymer chain and the primary hydroxy groups of starch.



Comparison of mechanical characteristics of the mixtures suggests that the co-polymers containing anhydride fragments react more strongly with starch (Table 3).⁷⁶ The breaking strength of starch–SMA mixtures is lower than that of pure SMA or PS but higher than that of starch–PS mixtures. In EPMA-containing compositions, the increase in the starch content up to 70 mass % increases the breaking strength of the systems. The increased resistance of starch mixtures with polymers containing anhydride groups is a result of enhanced interphasic adhesion at the boundary between the structural inhomogeneities caused by the reaction of the anhydride groups of the synthetic polymer with the hydroxy groups of starch.

Table 3. The breaking strengths of polymers and polymer–starch mixtures.⁷⁶

Sample	Starch:co-polymer ratio	σ_p /MPa
SMA		33.2
Starch–SMA	60:40	18.4
	70:30	17.7
PS		31.0
Starch–PS	60:40	9.6
EPMA		6.2
Starch–EPMA	60:40	6.4
	70:30	8.3
EP		> 8.9
Starch–EP	70:30	2.8

Starch mixtures with EPMA and SMA are easy to mould, display satisfactory mechanical characteristics and are biodegradable by spores of the fungus *Penicillium funiculogum*, which is facilitated with an increase in the starch content. At low starch content, starch granules remain encapsulated within the synthetic polymer and are thus hardly accessible to microorganisms.⁷⁶

Starch–EPMA and starch–SMA films are highly hydrophilic. Adsorption of water by these specimens depends on the method for the preparation of the mixtures and the moulding regime, since mechanical action induces decomposition of starch granules. Both compositions are rather resistant to water at room temperature despite high starch content (50 mass %–80 mass %); after keeping in water for two months, they absorb as little as 10 mass %–30 mass % of H₂O. The resistance of starch mixtures with EPMA to water under conditions mimicking sterilisation (121 °C, 10 min) is higher than that of starch mixtures with SMA.⁷⁶

Using scanning electron microscopy, it was shown⁷⁸ that a material possessing good mechanical properties can be prepared by varying the compositions of three-component mixtures (starch–SMA–EPMA) and moulding conditions. Starch granules in this material have a size of 1 to 5 µm.

A thermoplastic material was obtained⁸⁰ by extrusion of a mixture of wheat, potato, corn or rice starch (36 mass %) with an ethylene–acrylic acid co-polymer (used as ammonium salt, EAA, 41 mass %), water (12.5 mass %), urea (8.4 mass %) and polyethylene glycol (PEG, 2,1 mass %). Mechanical characteristics of films depended on the origin of starch as well as on the contents of water and PEG. The films based on wheat starch possessed the highest values of the elasticity modulus (~180 MPa). The mechanical characteristics deteriorate with an increase in the concentration of the plasticiser.

Thermooxidation resistance of mixtures of low-pressure polyethylene (LPPE) with a methyl methacrylate–butadiene–styrene co-polymer (MBS), with EAA and plasticised starch at 190 °C was studied^{81–83} using thermogravimetry, DSC and IR spectroscopy both upon continuous heating and in the isothermal regime. It was shown that MBS and EAC accelerate, whereas starch

decelerates thermooxidation of LPPE. A ternary LPPE–EAA–starch system appeared to be the most resistant to temperature, apparently due to the stabilising effect of the co-polymer at the PE–starch interface.

2. Mixtures of starch with cellulose derivatives and other natural polymers

A great number of investigations of the past decade^{84–92} were devoted to studies of starch mixtures with other natural polymers, such as pectins, cellulose, *etc.*, or products of their chemical modification. The feasibility of production of biodegradable packaging films for food stuffs as well as for biomedical purposes from starch–gutta-percha mixtures was studied by Arvanitoyannis *et al.*⁸⁴

Biodegradable starch mixtures with natural water-soluble polysaccharides, *viz.*, pectins, were studied^{85–87} using dynamic mechanical analysis, dilatometry, scanning electron microscopy and IR spectroscopy. Plant cell wall pectins contain esterified polygalacturonic acid residues, the degree of esterification depending on the origin of pectin. The pectins studied were isolated from citrus plants, sugar beet, almonds and water-melon rinds.^{85–87} The rupture strength and elasticity modulus of films cast from aqueous solutions practically do not depend on the origin of pectin. The rupture strengths of glycerol-plasticised films of pectin–starch mixtures change only slightly with an increase in the plasticiser content up to 45 mass %. Further increase in the glycerol content up to 75% sharply decreases the rupture strength and increases 10-fold the chain elongation at break. The increase in the starch content in the mixtures attenuates the plasticising effect of glycerol and thus makes the films more rigid. The level of mechanical properties of pectin–starch–glycerol films correspond to the mean values of the mechanical characteristics of films prepared from ordinary synthetic polymers ($\sigma_p = 27$ MPa, elasticity modulus 2×10^3 – 3×10^3 MPa). A change in the dynamic strain at a constant frequency of 1.6 Hz over a broad range of temperatures (from -100 to -200 °C) causes the appearance of three regions of mechanical relaxation, *viz.*, at -50 , 25 and ~ 100 °C. The position of mechanical losses peaks depends on the amount of the plasticiser (glycerol) added, *viz.*, the transition temperature decreases with an increase in the glycerol concentration. Using IR spectroscopy, it was shown⁸³ that the position of the band corresponding to the carboxy group of pectin changes noticeably after addition of glycerol, whereas the positions of the absorption bands characteristic of starch change to a lesser degree. The results of spectral studies⁸³ suggest that plasticised films prepared from starch mixtures are highly compatible with pectin. However, phase homogeneities of the systems under study were not proved.

Extrusion of corn starch mixtures with microcrystalline cellulose and methyl cellulose (MC) in the presence of additives, *e.g.*, plasticisers (polyols), or without them was used to produce edible films.⁸⁸ The increase in the concentration of the cellulose component increases the rupture strength and decreases the elongation at break and the permeability of films for water vapour.

Thermoplastic films plasticised with triacetyl glycerol were obtained by hot moulding of mixtures of potato or corn starch with cellulose diacetate (CDA).⁸⁹ The ratio of the polymeric components in the mixtures was varied at a constant concentration of triacetyl glycerol (35 mass %) relative to the total polymer mass. It was shown that the effective viscosity of the mixture decreases with an increase in the starch content from 10 mass % to 80 mass %, while the fluidity index of the melt increases from 2 to 70 g within 10 min, which was interpreted as an increase in the plasticiser content relative to CDA with a rise in the starch content in the system. Potato starch forms more viscous compositions with CDA than corn starch.

Commercial plasticised films were prepared from starch–CDA mixtures by injection moulding.⁹⁰ In their mechanical properties, these films are similar to polystyrene films but are additionally biodegradable. In these mixtures, biodegradation

first affects starch and the plasticiser and only afterwards involves CDA. The compositions containing starch and cellulose acetate are unstable in sea water but can be used as biodegradable non-toxic plastics for short-term use in air.

Using static sorption of water vapour, it was shown^{91,92} that water-soluble starch forms mixtures with MC and carboxymethylcellulose (CMC), which are thermodynamically compatible if the starch content is below 25 mass %; with an increase in the starch content, the systems become microheterogeneous. The rate of biodegradation of such films by microorganisms in water–soil suspensions as determined by the evolution of carbon dioxide depends on the degree of swelling and solubility of the components of the polymeric mixture in water, which facilitates their biodegradation. The rate of biodegradation of MC and CMC mixtures with starch in aqueous media does not depend on the phase state of the system and increases with an increase in the starch content.

Starch mixtures with ternary co-polymers based on caprolactam, dodecalactam and salts of adipic or sebacic acids with hexamethylene diamine were obtained by compression moulding.⁹³ The mixtures of components containing up to 30 mass % of starch are compatible as evidenced from the negative iodine test and the presence of a single relaxation dielectric loss peak around 50 °C. The resistance of these mixtures to water depends on the number of non-polar methylene groups between the amide bonds of the co-polymer. In systems with the same content of starch, the stability of the mixture containing a dodecalactam-based co-polymer is higher. The biodegradation of these films in water, as in the majority of starch-containing mixtures, is facilitated with an increase in its concentration in the system.

Extrusion of a mixture of starch, EVAI and inorganic compounds, *e.g.*, hydroxyapatite, was used to obtain biodegradable materials.⁹⁴ These compositions contain more than 30 mass % of natural or synthetic hydroxyapatite and resemble bone both in exterior and in mechanical properties. Scanning electron microscopy and X-ray diffractometry data testify to the homogeneity of their microstructure.

All the polymeric mixtures mentioned above could find practical application in the future. The thermoplastic materials (*e.g.*, Mater Bi, Novon, Bioflex) manufactured in Italy, USA, Canada and Germany (predominantly for ‘fast food’ enterprises) provide examples of commercial compositions based on starch.^{7,95–97}

Novon, a thermoplastic material prepared from plasticised starch, usually contains modified derivatives of polysaccharides.

Mater Bi represents a mixture of starch with polycaprolactone or EVAI and usually contains glycerol as the plasticiser.

The materials prepared from these compositions are highly stable and compete favourably with PE films in mechanical properties.^{96,97} The films prepared by extrusion and blowing can be used in the production of plastic bags for carrying small loads (~ 3 to 5 kg).

The biodegradability of Mater Bi materials under aerobic and anaerobic conditions in water and in compost has been studied in detail.⁹⁵ It was shown that the plasticiser is washed out rapidly in aqueous media. The starch : polycaprolactone ratio remains constant (54 : 46) under aerobic conditions during biodegradation with bacteria; under anaerobic conditions, the biodegradation predominantly affects starch.

3. Chemical modification of starch

Yet another method for the preparation of starch-based materials is chemical modification of starch, which consists in polymer-analogous transformations (most commonly, by esterification of the hydroxy groups) or introduction of fragments of different chemical origin into the polysaccharide macromolecule (*e.g.*, the synthesis of the so-called graft co-polymers). In this review, we shall consider the properties of the compositions containing the products of polymer-analogous conversions of starch and their mixtures with other polymers.

Starch acetates differing in the degree of substitution (from 1.5 to 2.5) were obtained from high-amylose corn starch.⁹⁸ According to DSC data, their T_g values changed from 165 to 185 °C; after plasticisation with water, T_g decreased to 35–95 °C. Extrusion of highly substituted starch acetate containing 15 mass % of water was used to obtain foamed materials, which surpassed foamed polystyrenes in plasticity and stability on compression. It is assumed⁹⁸ that such materials can be used in the production of packaging materials for agricultural and food industries.

Mechanical properties of films prepared from acetylated starch are determined by the origin of starch,⁹⁹ being dependent on the content of amylose and amylopectin in the original polymer.¹⁰⁰ The films with a high content of branched amylopectin acetate display high rupture strengths but are fragile.¹⁰⁰

Starch acetates are much less hygroscopic than non-modified starch.¹⁰⁰ Using four samples of acetylated corn starch with a fixed (from 3.3 mass % to 66 mass %) content of amylose as examples, it was shown that esterification increases the solubility and swelling capacity of starch in organic media.⁹⁹ Acetylated starch gels are less rigid and more elastic and transparent than the gels formed by the original starch. The low-amylose starch acetate is an exception. However, in contrast to native starch, the acetylated products are less biodegradable, since esterification prevents the action of enzymes on starch.⁹⁹

Mixtures of acyl derivatives of starch with yet another biodegradable polymer, viz., poly-3-hydroxybutyrate (PHB), are highly recommended as candidates for starch compositions.¹⁰¹ The components of the polymeric composition are incompatible as evidenced from the independence of the positions of their characteristic absorption bands in the IR spectra on their ratio. However, the temperature and enthalpy of melting of partially crystallised PHB decrease after the addition of starch acetate, which affects the morphological properties of PHB crystallites and increases its ability for crystallisation.

Carboxymethyl starch was obtained by treatment of yellow corn starch and pigweed starch (the degree of substitution = 0.1–0.2) with chloroacetic acid.¹⁰² Small additions of carboxymethyl starch were used for the extrusion of various food stuffs derived from semolina. It was found that modified starch improves processing of these products.

Elastic edible films were prepared from hydroxypropyl starch mixed with gelatine and plasticised with polyols and water (up to 25 mass %) by Arvanitoyannis *et al.*¹⁰³ The permeability of these films for oxygen and CO₂ increases with an increase in the content of the plasticiser in the system, which deteriorates the quality of packaging materials for food stuffs.

Higher fatty acid esters of starch are promising reagents for mixing with non-polar polymers, such as PE and polypropylene.¹⁰⁴ The reaction of starch with the corresponding acid chlorides in DMSO gave starch octanoates and dodecanoates with the degree of substitution of 1.8 and 2.7. The ester groups containing higher alkyl radicals improve the affinity of starch for the non-polar synthetic polymer and act as internal plasticisers. The compatibility of starch dodecanoate with PE is higher than that of starch octanoate. The starch dodecanoate–PE mixtures manifest higher thermal stabilities, greater elongation at break upon rupture and lower moisture absorption than starch octanoate–PE mixtures. However, being introduced into PE at any ratios, these substances decrease the rate of biodegradation of the mixture in comparison with starch–PE mixtures.

Starches modified by the introduction of cholesterol residues¹⁰⁵ and mixed with high-pressure PE were used for the production of blown films. In comparison with non-modified starch, these materials are more homogenous and more stable. Biodegradation in a compost of films prepared from these mixtures occurs even faster than that of non-modified starch–PE mixtures, apparently due to the loosening of the starch structure caused by bulky cholesterol fragments.

The preparation and investigation of properties of the systems based on chemically modified starch has found lesser application

than the preparation of systems from mixtures of native starch with other polymers.

V. Conclusion

Studies carried out in the past decades have demonstrated that biodegradable materials should combine high mechanical and other essential operational and technological properties (*e.g.*, stability, low gas permeability, environmental safety, easy moulding, *etc.*) with biodegradability. Biodegradable materials based on starch or starch mixtures with synthetic polymers are the most readily available and have found wide practical application.

The properties of starch-based polymeric materials including their biodegradability depend on the compatibility of the mixture components and the structure of the systems thus prepared. However, the thermodynamic and energetic characteristics of the interaction of starch with synthetic polymers within the mixtures and the structure of such systems are still poorly known. It is these properties of starch mixtures with synthetic polymers that must be subject of comprehensive analysis in order to establish the general regularities with the ultimate goal to select the components and technologies for the preparation of polymeric materials, which are stable in various media and biodegradable.

The widening of the range of biodegradable polymeric systems is very important for future studies; therefore it is hoped that the results described in this review will be useful for further studies based on the use of this environmentally important scientific approach.

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^a — *Polym. Sci. (Engl. Transl.)*

Synthesis and properties of nitrogenous heterocycles containing a spiro-fused cyclopropane fragment

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Abstract. The published data on the methods of synthesis and chemical transformations of nitrogenous heterocyclic compounds spiro-fused with a cyclopropane fragment are described systematically and generalised. The bibliography includes 146 references.

I. Introduction

Synthesis and studies of the properties of highly strained carbocyclic compounds, including those incorporating a cyclopropane ring, is a field of organic chemistry which is developing most intensely. Today, many methods for the synthesis of cyclopropanes are known; their chemical transformations have been studied, and diverse spheres of practical use of these compounds have been found by now. The introduction of a spiro-fused cyclopropane fragment in a heterocyclic molecule changes the reactivity of the heterocycle. The high strain of the three-carbon ring predetermines its ability to undergo facile opening with a change in the spiro-carbon atom hybridisation from sp^3 to sp^2 . Since heterocyclic compounds (including mono- and polynitrogen-containing ones) find use as medicines and as chemical means for plant and animal protection, synthesis of their analogues with a spirocyclopropane fragment is interesting both from the theoretical viewpoint and for the preparation of new biologically active compounds, in particular, potential pharmaceuticals.

Synthesis of heterocycles containing a spiro cyclopropane fragment involves either the formation of a heterocyclic structure from compounds that already possess a three-carbon ring or the formation of a cyclopropane ring in structures incorporating the required heterocycle. The first approach is primarily based on various [3 + 2]- and [4 + 2]-cycloaddition reactions that can be carried out using either cyclopropane-containing dipolarophiles (dienophiles), e.g., methylenecyclopropanes, or nitrogen-containing 1,3-dipoles or dienes in which one atom of the cyclopropane ring is involved in the reactive fragment. Diazocyclopropane generated *in situ*, which readily reacts with

certain unsaturated compounds to give spiro[cyclopropanedihydropyrazoles], is a promising building block of the latter type.

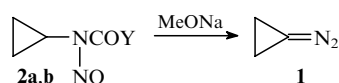
The second approach is based on the addition of aliphatic diazo compounds to the activated exocyclic double bond in a heterocycle followed by dedinitrogenation of the resulting dihydropyrazoles, as well as on the addition of carbenes or ylides to methylenesubstituted heterocycles.

This review is a first attempt at generalisation of the published data on the synthesis and some chemical transformations of heterocyclic compounds incorporating a spirocyclopropane fragment and at least one nitrogen atom in the ring. The presented material is mostly arranged according to the class of the key compounds used for the construction of the spirocyclopropane-containing azaheterocycles. The structures in which the cyclopropane fragment is not spiro-fused directly with the azaheterocycle are not considered.

II. The formation of nitrogen-containing heterocyclic systems from compounds with a cyclopropane fragment

1. Cycloaddition involving diazocyclopropane

Diazocyclopropane (**1**) is a promising compound for the synthesis of compounds incorporating a spiro-fused cyclopropane fragment which are difficult to access.^{1–4} Generally, diazocyclopropane (**1**) is generated by decomposition of *N*-cyclopropyl-*N*-nitrosourea (**2a**)^{1,4} or *N*-cyclopropyl-*N*-nitrosocarbamate (**2b**)^{2,3} on treatment with strong bases, by analogy with the synthesis of aliphatic diazo compounds.⁵ Unlike the majority of the known aliphatic and cyclic diazo compounds, both diazocyclopropane (**1**) and all of its derivatives mentioned in the literature^{6–9} are quite unstable compounds which have not been detected in individual form. Nevertheless, the formation of diazocyclopropanes *in situ* follows from the methods used for their generation and chemical trapping. For example, its reactions with unsaturated compounds result in 1,3-dipolar cycloaddition products, *viz.*, the corresponding spiro[cyclopropane-4,5-dihydro-3*H*-pyrazoles].



Y = NH₂ (**a**), OEt (**b**).

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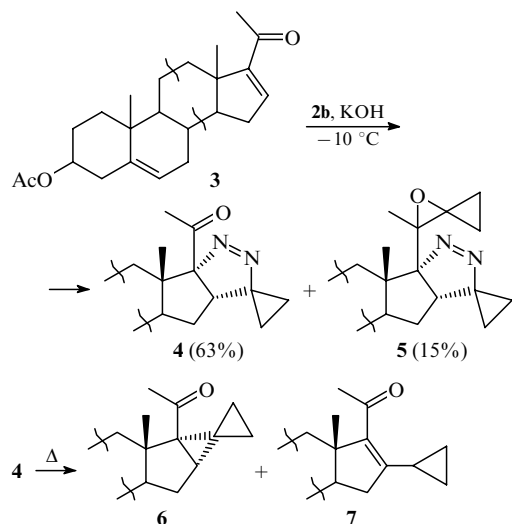
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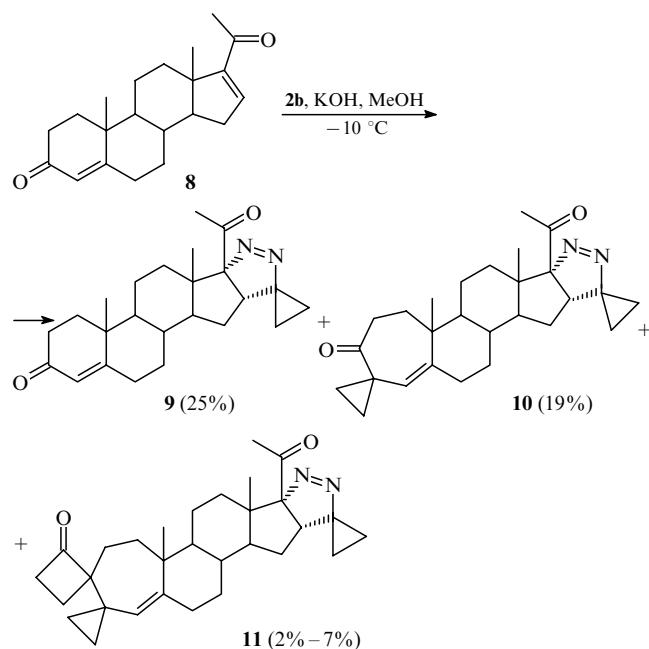
Uspekhi Khimii 69 (6) 507–527 (2000); translated by S S Veselyi

The reaction of diazocyclopropane (**1**) with oxosteroids^{2,3} should be noted as one of the first examples of the trapping of compound **1** with unsaturated compounds. For example, diazo-

cyclopropane (**1**) generated *in situ* undergoes selective addition to the Δ^{16} bond of the diene **3** to give dihydropyrazole **4**. The reaction of an excess of the diazo compound **1** with the carbonyl group of the adduct **4** results in oxaspiropentane **5**. Thermolysis² of the dihydropyrazole **4** isolated in individual form, as in the case of similar dihydropyrazoles obtained by the addition of other diazoalkanes,¹⁰ occurs non-selectively: in addition to the usual reaction product, *viz.*, the spirocyclopentane derivative **6**, the β -substituted α,β -enone **7** is formed (the ratio **6**:**7** is 3.5:1).

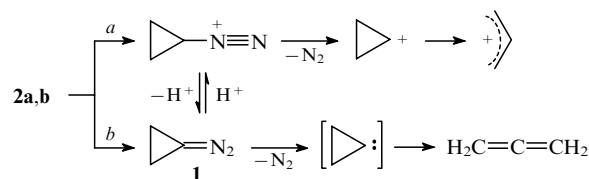


It should be noted that the reaction of diazocyclopropane (**1**) with the cyclohexenone fragment of steroids under the same conditions occurs in a different way.³ For example, the reaction of compound **8** gives not only the expected addition product to the Δ^{16} bond, *i.e.*, the adduct **9**, but also compound **10** due to the six-membered ring expansion, which is similar to homologisation of cyclic ketones on treatment with diazomethane.¹¹ Cyclobutanone **11** formed upon formal addition of cyclopropylidene to the carbonyl group of the cycloheptane fragment of compound **10**³ was identified as a minor product.



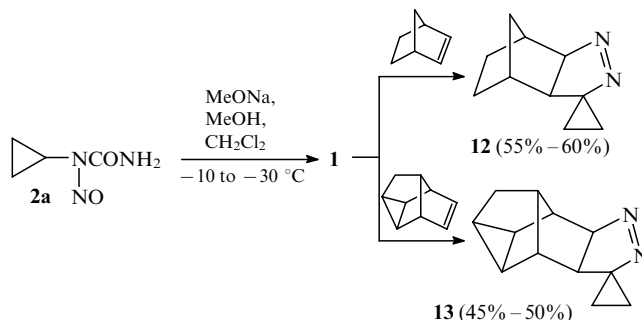
Although diazocyclopropane (**1**) can in principle be trapped by alkenes to give spiro[cyclopropanedihydropyrazoles], this reaction did not find synthetic application for a long time, primarily because the nature of unsaturated substrates which can enter into 1,3-dipolar cycloaddition with compound **1** was not

determined with certainty. In fact, there are several examples where generation of diazocyclopropane (**1**) in the presence of unsaturated compounds, such as cyclohexa-1,4-diene,¹² bicyclopentylidene,¹³ or cycloalkyl-substituted bicyclopentylidenes,^{14–16} resulted in spirane hydrocarbons rather than dihydropyrazoles which were formed due to [1 + 2]-cycloaddition of cyclopropylidene to these compounds. Generation of diazocyclopropane from compounds **2a,b** can produce, in addition to cyclopropylidene, other unstable species. The pathways of transformation of cyclopropyl nitrosourea **2a** and cyclopropyl nitrosoureas substituted at the cyclopropane ring on treatment with reagents of different basicity and nucleophilicity were studied in a series of works by Kirmse *et al.*^{1,17–27} It was assumed that their reactions give rise to cyclopropyldiazonium salts, as well as cyclopropyl and allyl cations due to the dedinitrogenation of these salts.

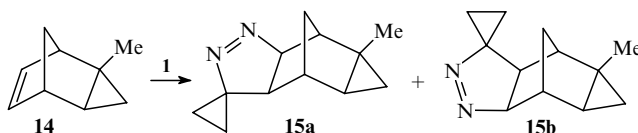


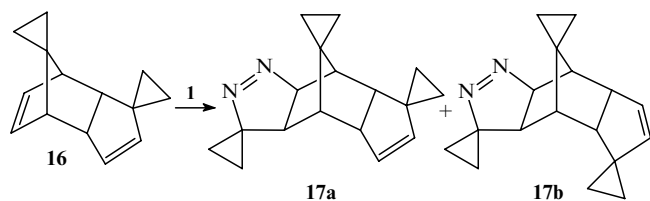
(a) weak base; (b) strong base.

Systematic studies of 1,3-dipolar cycloaddition of diazocyclopropane (**1**) to alkenes, first of all a systematic search for efficient traps for compound **1** to give spiro[cyclopropanedihydropyrazoles], date back to the beginning of the 1990s. It was found that reactions of diazocyclopropane (**1**), generated *in situ* on treatment of cyclopropyl nitrosourea (**2a**) with sodium methoxide, with norbornene⁴ and other compounds containing the bicyclo[2.2.1]heptene fragment²⁸ mostly result in spiro[cyclopropanedihydropyrazoles] of the types **12** and **13**, exclusively as *exo*-isomers. Good yields (50%–70%) are achieved if a molar excess as low as 1.5-fold of the unsaturated substrate with respect to cyclopropyl nitrosourea (**2a**) is used.

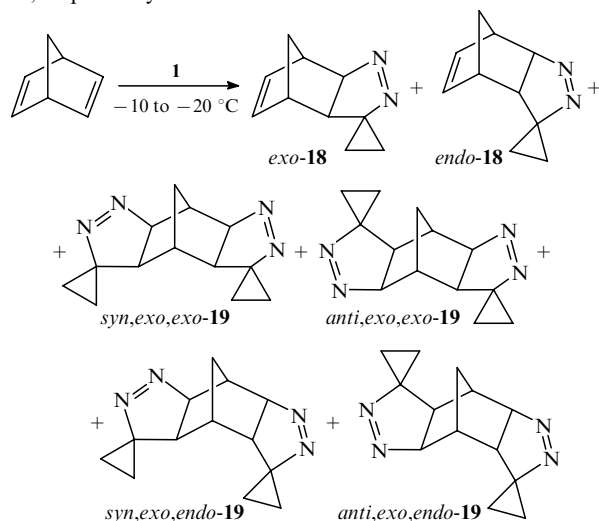


The asymmetrically substituted hydrocarbon **14** gives a mixture of isomeric spiro[cyclopropanedihydropyrazoles] **15a** and **15b** due to the different approach of diazocyclopropane to the double bond; their ratio was ~1:1 and the overall yield was 55%–58%. The polycyclic diene **16** reacts with diazocyclopropane (**1**) in a similar way.²⁸ Despite the steric hindrance created by the spirocyclopropane fragment in the norbornene moiety, dihydropyrazoles **17a** and **17b** (in a ratio ~1.4:1) are also formed exclusively as *exo*-isomers, although their overall yield (23%) is markedly lower than that of norbornene unsaturated at position 7. It should be noted that this reaction did not give any addition products of diazocyclopropane (**1**) (or cyclopropylidene) to the cyclopentene double bond.



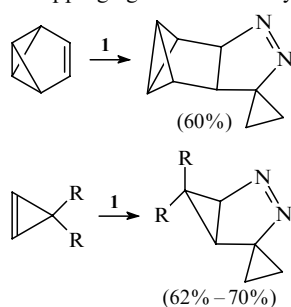


The reaction of norbornadiene with diazocyclopropane (**1**) generated *in situ* also occurs as 1,3-dipolar cycloaddition, although less selectively, and results in a mixture of isomeric mono- (**18**) and bisadducts (**19**) in 32%–35% and 35%–38% yields, respectively.⁴



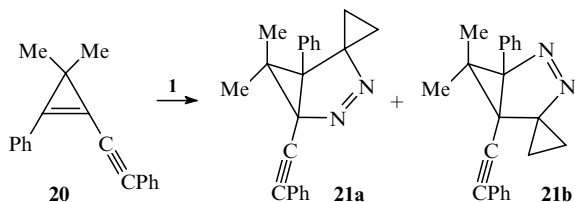
Unlike the adducts **12**, **13**, **15** and **17**, monospiro[cyclopropanedihydropyrazoles] **18** are a mixture of *exo*- and *endo*-isomers in the ratio $\sim 4:1$, while the bisadducts **19** formed from them are a mixture of four isomers in the ratio $\sim 10:7:1.3:1$. Although a two-fold excess of norbornadiene is used, bisadducts **19** are formed in an even greater quantity than monoadducts **18**; the addition of the second diazocyclopropane molecule to monoadducts **18** occurs exclusively at the *exo* position.

Benzvalene and 3,3-disubstituted cyclopropenes are also efficient trapping agents for diazocyclopropane (**1**).^{4, 28, 29}



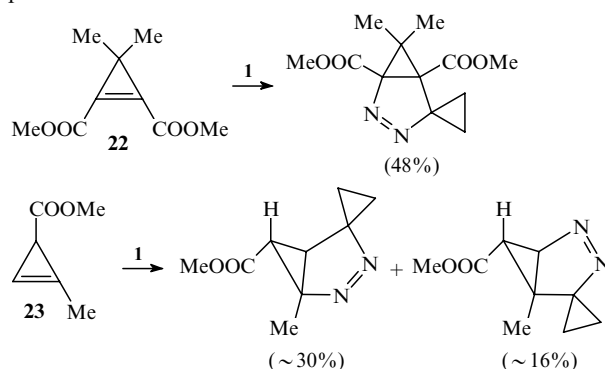
R = Me; R–R = (CH₂)₃.

The reaction of diazocyclopropane (**1**) with alkynylcyclopropane **20** results in regioisomeric dihydropyrazoles **21a** and **21b** in the ratio $\sim 3:1$; this reaction does not involve the triple bond.²⁹



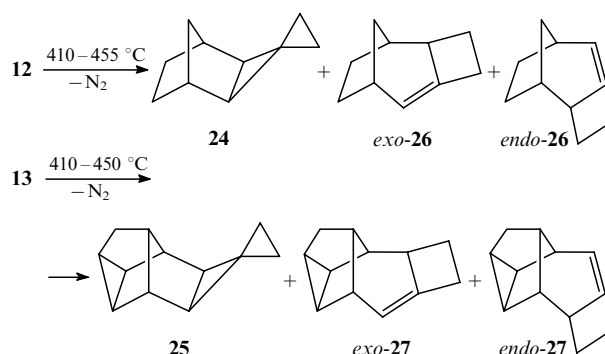
1,3-Dipolar cycloaddition products are formed in reactions of diazocyclopropane (**1**) with methyl cyclopropenecarboxylates **22**

and **23**.^{28, 29} The regioselectivity is low in the case of the cyclopropene **23**.

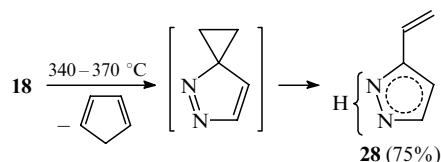


In the synthesis of dihydropyrazoles from cyclopropenes **20** and **22**, alternate addition of cyclopropylnitrosourea (**2a**) and the corresponding cyclopropene to a suspension of MeONa in a MeOH–ether mixture at -20 to -30 °C was found to be the method of choice.²⁹

It should be noted that the majority of the resulting polycyclic spiro[cyclopropanedihydropyrazoles] possess rather high thermal stability.³⁰ For example, dihydropyrazoles **12** and **13** are stable when heated to 200 °C. In the gas phase at 410–450 °C, they undergo dedinitrogenation to give a mixture of strained hydrocarbons, *viz.*, spiro[tricyclo[3.2.1.0^{2,4}]octane-1,3'-cyclopropane] (**24**) or spiro[pentacyclo[4.4.0.0^{2,8}.0^{3,5}.0^{7,9}]decane-4,1'-cyclopropane] (**25**), as well as isomeric compounds **26** or **27** containing a fused cyclobutane fragment (overall yield 30%–70%). An increase in temperature favours the isomerisation of the spirane hydrocarbons **24** and **25** to the corresponding unsaturated compounds **26** and **27**.

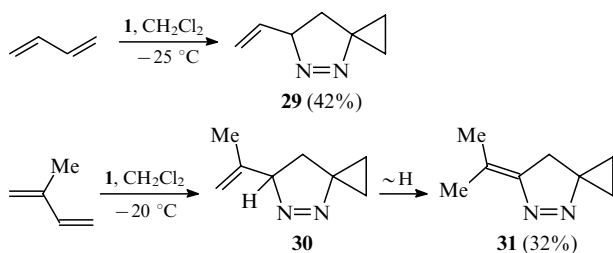


The unsaturated 4,5-dihydro-3*H*-pyrazole **18** obtained by the addition of diazocyclopropane (**1**) to norbornadiene eliminates cyclopentadiene instead of N₂ on thermolysis to give 3(5)-vinylpyrazole (**28**).³⁰

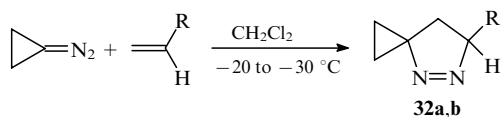


In addition to strained cyclic unsaturated compounds, conjugated aliphatic dienes such as buta-1,3-diene can also play the role of trapping agents for diazocyclopropane (**1**).²⁸ At -25 °C, 6-vinyl-4,5-diazaspiro[2.4]hept-4-ene (**29**) is formed as the major product; unlike polycyclic dihydropyrazoles, it readily undergoes polymerisation to give a rubber-like substance. The reaction of diazocyclopropane (**1**) with 2-methylbuta-1,3-diene also occurs as 1,3-dipolar addition, but 6-isopropylidene-4,5-diazaspiro[2.4]hept-4-ene (**31**) rather than 5-isopropenyldihydropyrazole **30** is formed in this case as the main reaction product. Apparently, the addition of diazocyclopropane occurs mostly to the unsubstituted

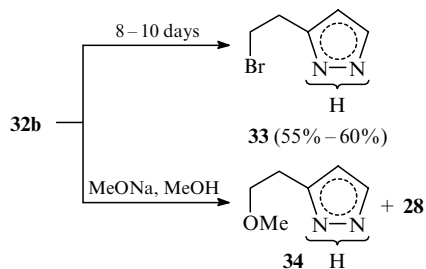
double bond, while the resulting dihydropyrazole **30** undergoes isomerisation under the reaction conditions.²⁸



It is well known that the reactivity of alkenes with respect to diazomethane and other aliphatic diazo compounds in 1,3-dipolar cycloaddition reactions is largely determined by the nature of the double bonds and that the reaction accelerates upon introduction of electron-withdrawing substituents.³¹ Successful 1,3-dipolar cycloaddition in the case of low-activity alkenes is usually provided by keeping the reaction mixture for a long time. This technique cannot be employed in reactions with diazocyclopropane because of its instability, which undoubtedly decreases the number of potential unsaturated partners of this reaction. It has recently been established that styrene³² and vinyl bromide³³ are rather good trapping agents for diazocyclopropane (**1**) generated *in situ*.³³ 1,3-Dipolar cycloadditions involving these alkenes occur regioselectively to give 5-phenyl- (**32a**) and 5-bromospiro[cyclopropane-1,3'-dihydropyrazoles] (**32b**), respectively. However, unlike the majority of spiro[cyclopropanedihydropyrazoles] considered above, including compound **32a**, bromodihydropyrazole **32b** is unstable and undergoes partial resinification and partial transformation to 3(5)-(2-bromoethyl)pyrazole (**33**) upon storage in an inert atmosphere at 15 °C for 8–10 days.³³ The reaction of the compound **32b** with MeONa in MeOH at 25 °C for 2 h results in a mixture of 3(5)-(2-methoxyethyl)- (**34**) and 3(5)-vinylpyrazoles (**28**) [overall yield ~ 80%, ratio (3–4) : 1].³³

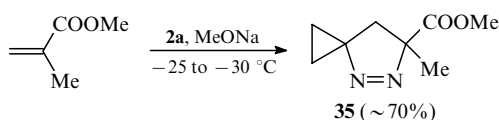


R = Ph (**a**, 67%), Br (**b**, 60%).

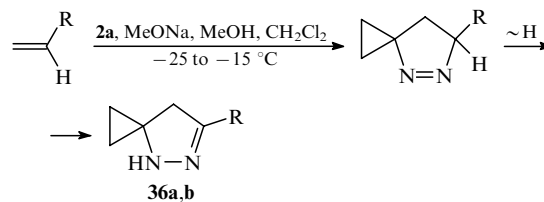


It should be noted that the reaction of diazomethane with vinyl bromide in ether readily results in pyrazole hydrobromide due to the facile dehydrobromination of the bromodihydropyrazole formed initially.³⁴ Thus, the spirocyclopropane moiety in the compound **32b** reduces the ability of the heterocyclic fragment to undergo deprotonation.

Acrylic acid derivatives are good substrates for reactions involving diazocyclopropane (**1**); for example, the addition of cyclopropylnitrosourea (**2a**) to a mixture of methyl methacrylate and sodium methoxide (ratio 1 : 1.5 : 1.5) affords dihydropyrazole **35** in a yield up to 70%.³⁵



Diazocyclopropane (**1**) reacts with acrylonitrile and methyl acrylate with equal efficiency. However, in this case the composition of the reaction products depends on the conditions and the reagent ratio.³⁶ In particular, generation of diazocyclopropane (**1**) by the addition of cyclopropylnitrosourea (**2a**) to a mixture of an unsaturated compound and MeONa in a solvent was found to be unacceptable due to a side reaction of methanol addition to the electron-deficient double bond of acrylonitrile or methyl acrylate. The side reaction can be inhibited almost completely by changing the order of addition of the reagents.³⁶ At the ratio **2a** : acrylate ~ 1 : 1, the expected spiro[cyclopropane-1,5'-4,5-dihydro-1*H*-pyrazoles] **36a,b** are formed as the main reaction products (yields ~ 70%).³⁶

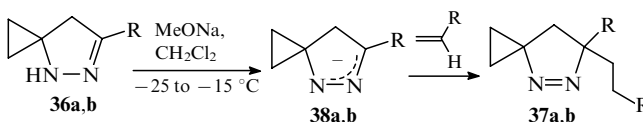


R = CN (**a**, 70%), COOMe (**b**, 69%).

It was shown later³⁷ that the synthesis of dihydropyrazole **36a** can be carried out with equal success with the use of K₂CO₃ instead of MeONa, but in this case complete decomposition of cyclopropylnitrosourea (**2a**) at 0–5 °C takes as long as 1–2 h.

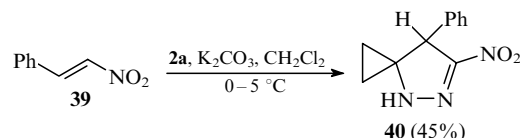
Dihydropyrazoles **36a,b** (especially **36b**) are rather labile compounds which undergo partial decomposition even under the conditions of preparative TLC.

An increase in the amount of acrylonitrile or methyl acrylate to 2–2.5 equiv. with respect to cyclopropylnitrosourea decreases the fraction of dihydropyrazoles **36a,b** to ~ 15% and results in new reaction products, *viz.*, functionally substituted dihydropyrazoles **37a,b**, which, as shown in special experiments,^{36–38} are formed upon reaction of dihydropyrazoles **36a,b** with the excess of unsaturated substrates. The generation of the anions **38a,b** is probably the driving force of the observed transformations. This procedure makes it possible to obtain spiro[cyclopropanedihydropyrazoles] containing functional substituents in the side chain and in the dihydropyrazole ring (see Section III).

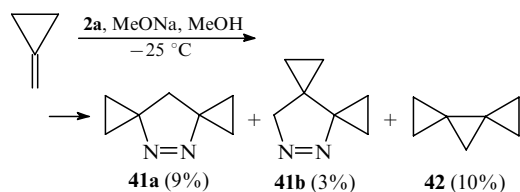


R = CN (**a**, 84%), COOMe (**b**, 80%).

Diazocyclopropane (**1**) undergoes regioselective addition to *trans*-β-nitrostyrene (**39**) to give 3-nitro-4-phenylspiro[cyclopropane-1,5'-4,5-dihydro-1*H*-pyrazole] (**40**).³⁷

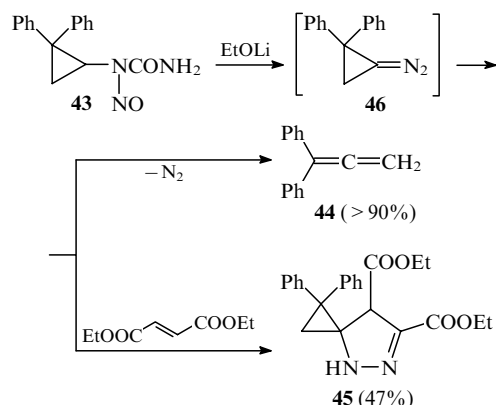


1,3-Dipolar cycloaddition of diazocyclopropane (**1**) to phenyl vinyl sulfide,³⁸ divinyl ether³⁷ and methylenecyclopropane⁴ occurs with low efficiency (the yields of dihydropyrazoles are 5%, 13% and 12%, respectively). The reaction with methylenecyclopropane gave a mixture of two regioisomers **41a,b** in the ratio ~ 3 : 1; in addition to dihydropyrazoles, the reaction of cyclopropylidene with methylenecyclopropane also gave dispiro[2.0.2.1]heptane (**42**). As it could be expected, cyclopropyl methyl ether and allene were the main side products of decomposition of cyclopropylnitrosourea (**2a**).⁴



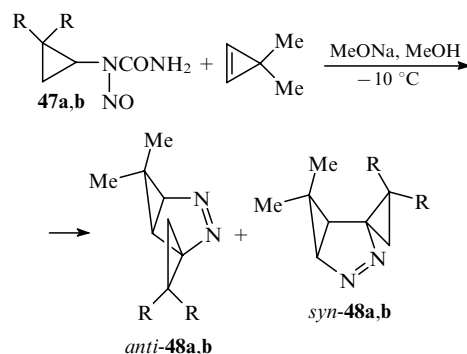
2. Cycloaddition involving substituted diazocyclopropanes

Along with the cycloaddition of diazocyclopropane (**1**) generated *in situ* to the unsaturated compounds considered above, there are examples of [3 + 2]-cycloaddition of substituted diazocyclopropanes to activated C=C bonds. For example, in the beginning of the 1960s, American authors obtained *N*-(2,2-diphenylcyclopropyl)-*N*-nitrosourea (**43**) and studied its decomposition in the presence of bases or on heating.^{7, 39, 40} On treatment with lithium ethoxide in saturated hydrocarbons, nitrosourea **43** is decomposed with evolution of N_2 but without the yellow coloration typical of diazo compounds; this reaction gives 1,1-diphenylallene (**44**) in high yield. In the presence of diethyl fumarate, the corresponding dihydropyrazole **45** is formed upon 1,3-dipolar cycloaddition of 2,2-diphenyldiazocyclopropane (**46**) to the double bond.⁷



Thermal decomposition ($60\text{--}82^{\circ}\text{C}$) of nitrosourea **43** in heptane or in an excess of diethyl fumarate results in the same compounds **44** and **45** (yields 95% and 44%, respectively);⁴⁰ this is untypical of other *N*-alkyl-*N*-nitrosamides.

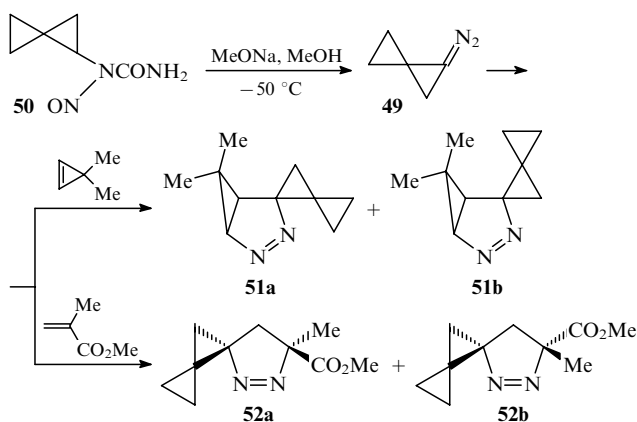
The reaction of 2,2-dimethyl- and 2,2-dichlorodiazocyclopropanes, generated *in situ* from the corresponding *N*-nitroso-*N*-cyclopropylureas **47a,b**, with a reactive dipolarophile, *viz.*, 3,3-dimethylcyclopropene, was studied.⁸ In both cases, a mixture of two isomeric dihydropyrazoles was formed in $\sim 70\%$ yield; the ratio of the *anti* and *syn* isomers was 2.2 : 1 for compound **48a** and 1 : 1.3 for compound **48b**.



R = Me (a), Cl (b).

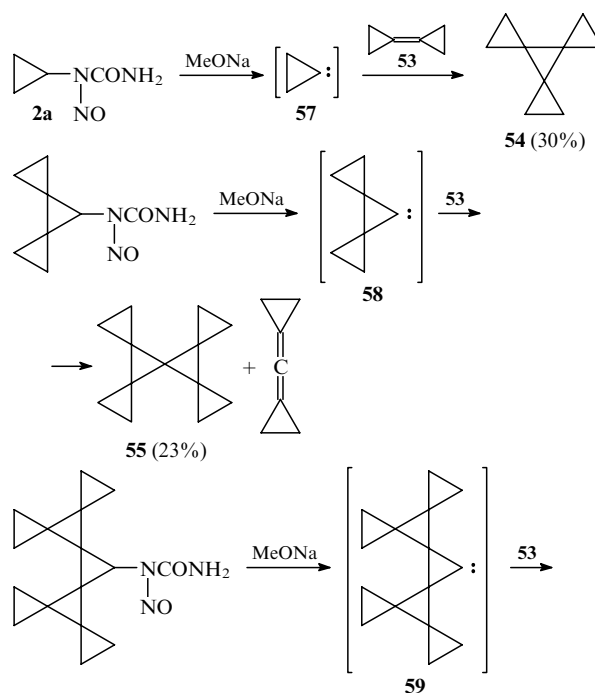
Generation of substituted diazocyclopropanes from substituted *N*-nitroso-*N*-cyclopropylureas is a promising method for the synthesis of nitrogenous heterocycles containing a polyspiran

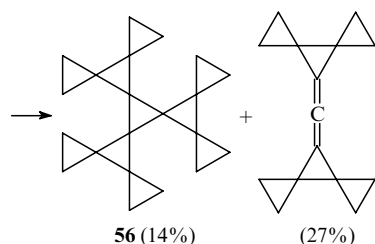
fragment. It has been shown recently^{9, 41, 42} that diazospirlopentane (**49**) generated *in situ* from *N*-nitroso-*N*-spiropentylurea (**50**) reacts with 3,3-dimethylcyclopropene or methyl methacrylate to give 4,5-dihydro-3*H*-pyrazoles **51a,b** or **52a,b** fused with the spiropentane fragment (as mixtures of isomers in the ratio $\sim 1 : 1$).



The yields of the 1,3-dipolar cycloaddition products **51** and **52** increase considerably with a decrease in the temperature of the reaction. For example, the yield of dihydropyrazoles **52** is $\sim 20\%$ at -20°C and increases to 72% at -50°C .⁹ Evidently, diazospirlopentane (**49**) is even less stable than diazocyclopropane (**1**).

Unlike strained cycloalkenes or alkenes with electron-withdrawing substituents, bicyclopopylidene (**53**) reacts with diazocyclopropanes generated *in situ* to give polyspirocyclopropane-containing hydrocarbons, in particular, triangulans **54–56**, instead of dihydropyrazoles ([3 + 2]-cycloaddition products).^{13–16, 43} Evidently, diazocyclopropanes cannot react with bicyclopopylidene (**53**) according to 1,3-dipolar cycloaddition due to a specific nature of the double bond in this compound, which manifests itself, in particular, in a noticeable shortening of this bond;⁴⁴ these compounds undergo dedinitrogenation to give the corresponding cyclopropylenes **57–59**, which are mostly isomerised into allenes. The reaction of cyclopropylenes **57–59** with the original bicyclopopylidene (**53**) occurs as [1 + 2]-cycloaddition to give triangulans **54–56**.



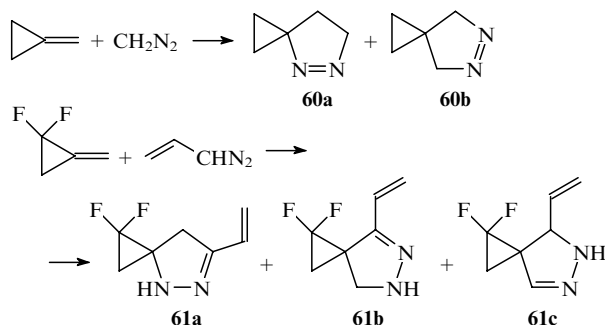


Diazocyclopropane and cyclopropylidene do not react with alkynes, such as $\text{PhC}\equiv\text{CH}$, $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$ and $\text{HC}\equiv\text{CC}(\text{Me})=\text{CH}_2$.^{29, 37}

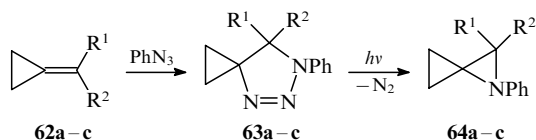
3. Cycloaddition to methylenecyclopropane and its derivatives

Syntheses of spirocyclopropane-containing azaheterocycles make use of cycloaddition of nitrogen-containing 1,3-dipoles to methylenecyclopropane and its derivatives with substituents both in the cyclopropane ring and at the double bond.

For example, the reaction of diazomethane with methylenecyclopropane at 3 °C for two weeks results in a mixture of two regioisomeric dihydropyrazoles **60a,b** (overall yield 90%, ratio 55 : 45).⁴⁵ The addition of diazomethane and 3-diazoprop-1-ene to 2,2-difluoromethylenecyclopropane also occurs non-selectively; a mixture of three regioisomeric 4,5-dihydro-1*H*-pyrazoles **61a–c** (~ 3.7 : 1 : 1) is formed in the latter case.⁴⁶



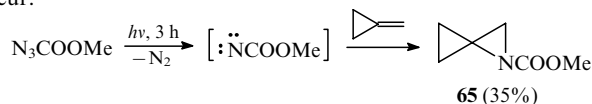
Phenyl azide slowly adds to methylenecyclopropane (**62a**), benzylenecyclopropane (**62b**) or (diphenylmethylenecyclopropane) (**62c**) to give the thermally stable spiro[dihydrotriazolecyclopropanes] **63a–c**. It is assumed^{47, 48} that the reaction occurs through a concerted mechanism with the addition of the terminal nitrogen atom of phenyl azide to the tetrasubstituted carbon atom of the cyclopropane ring. Photolytic dedinitrogenation of 4,5-dihydro-1*H*-1,2,3-triazoles **63a–c** (Pyrex, high-pressure mercury lamp) affords new azaheterocycles **64a–c**, which are derivatives of 1-phenylazaspiropentane (yields 90%, 99% and 90%, respectively).^{47, 48}



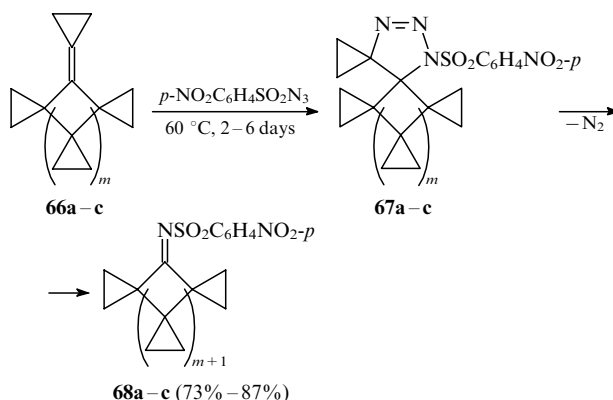
Compound	R ¹	R ²	T /°C	t /days	Yield of 63 (%)
a	H	H	20	60	70–80
			50	1	70–80
b	H	Ph	100	1–2	38
c	Ph	Ph	100	1–2	51

Apparently, the azaspiropentane fragment can also be formed upon direct addition of nitrenes to the double bond of methylenecyclopropanes. At least, this is how the photochemical reaction of methyl azidoformate with methylenecyclopropane

to give 1-(methoxycarbonyl)azaspiropentane (**65**) is believed to occur.⁴⁸



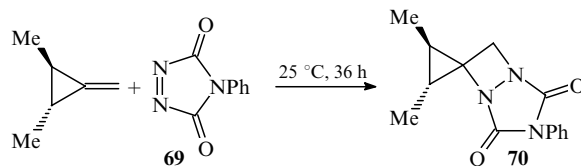
Unlike phenyl azide, cyanogen azide and *p*-nitrobenzenesulfonyl azide do not give any stable dihydrotriazoles in reactions with cyclopropylidenecycloalkanes: they readily undergo dedinitrogenation. The addition of cyanogen azide to cyclopropylidenecyclohexane (~ 20 °C, 7 days) probably occurs non-regioselectively, since hydrolysis of the reaction mixture gives spiro[2.6]nonan-4-one and spiro[3.5]nonan-1-one (yields 46% and 30%, respectively).⁴⁹ The reactions of *p*-nitrobenzenesulfonyl azide with cyclopropylidenepolyspiroalkanes **66** occur regioselectively *via* dihydrotriazoles **67** which readily undergo dedinitrogenation with simultaneous ring expansion to give imides **68**.^{50–52}



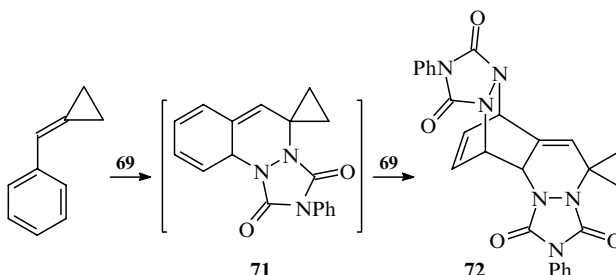
$m = 0$ (a), 1 (b), 2 (c).

Similarly, diazocyclopropane (**1**) probably adds to the imide **68a** *via* an unstable dihydrotriazole, which is transformed into the imide **68b**.⁵²

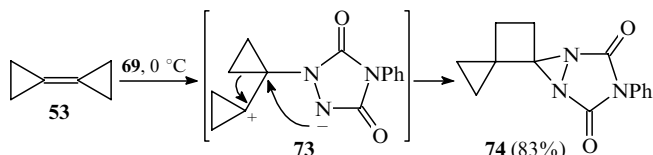
Diverse heterocyclic compounds containing a spirocyclopropane fragment are obtained by treatment of methylenecyclopropanes with dihydrotriazoledione **69**; the reaction pathway depends considerably on the nature of the substituents at the cyclopropane ring. In particular, [2 + 2]-cycloaddition of *trans*-2,3-dimethyl-1-methylenecyclopropane to dihydrotriazoledione **69** at room temperature to give the adduct **70** occurs slowly.⁵³



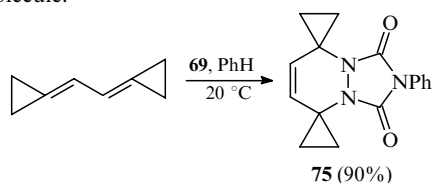
With benzylenecyclopropane, dihydrotriazoledione **69** reacts much faster. However, in this case compound **71** formed in the first step, *i.e.*, a product of formal [4 + 2]-cycloaddition involving the benzene ring of the substituent, contains a cyclohexadiene fragment and readily adds the second molecule of dihydrotriazoledione **69** to give the bisadduct **72**.⁵³



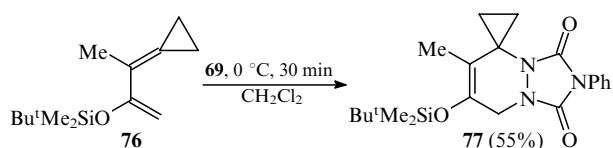
The cycloaddition of dihydrotriazolodione **69** to bicyclopopylidene (**53**) occurs in an unexpected way; simple closure of the four-membered heterocycle in the resulting zwitter-ion **73** does not occur in this case. After an alkyl shift, the carbon atom in the cyclopropane fragment that was involved in the formation of the first C–N bond is attacked by the nucleophilic nitrogen atom. Diaziridine **74** is the only reaction product that was isolated.⁵⁴



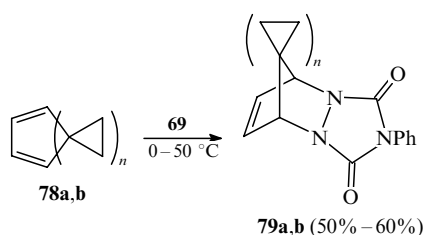
Unlike the methylenecyclopropanes considered above, conjugated alkenylidenecyclopropanes react with dihydrotriazolodione **69** as true dienes to give [4 + 2]-cycloadducts. For example, the reaction with bis(cyclopropylidene)ethane occurs almost instantaneously and gives high yield of the cycloadduct **75** where both cyclopropane fragments are retained in the molecule.⁵⁵



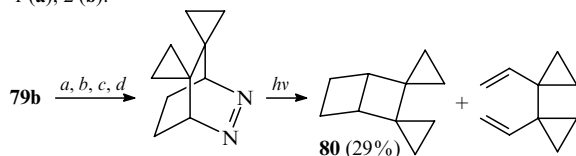
1-Methyl-2-silyloxyprop-2-enylidenecyclopropane (**76**) can act as a 1,3-diene in the reaction with the dihydrotriazolodione **69**, giving a heterocyclic compound **77** in 55% yield.⁵⁶



Synthesis of polycyclic heterocycles with a spirocyclopropane fragment in the molecule is carried out using the reaction of the dihydrotriazolodione **69** with cyclic dienes **78a,b** or with their derivatives. The [4 + 2]-cycloadducts **79a,b** are formed in high yields under mild conditions.^{57–61} Subsequent transformations of the heterocyclic adduct **79b** afforded highly strained dispiro[2.0.2.4]decane **80**.^{59, 60}



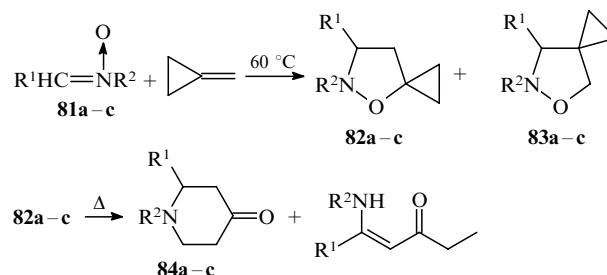
$n = 1$ (a), 2 (b).



(a) H_2 , Pd/C, MeOH; (b) Bu^tOK, DMSO, H_2O ;
(c) CuCl_2 , H_2O , EtOH; (d) KOH.

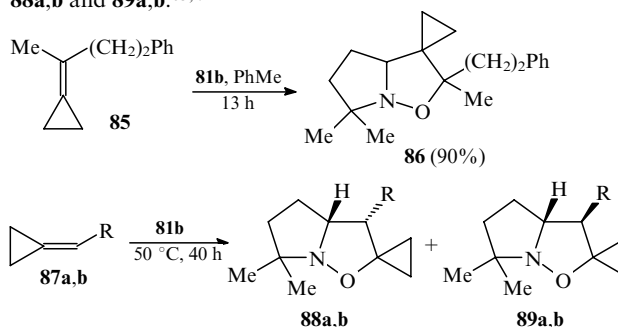
Both linear and cyclic nitrones can act as 1,3-dipolar compounds in reactions with methylenecyclopropanes.^{62–66} The reaction of methylenecyclopropane with nitrones **81a–c** occurs as [3 + 2]-cycloaddition with retention of the cyclopropane fragment; in this case, mixtures of regioisomers **82a–c** and **83a–c** are

formed in the ratio (2–9):1 in 69%–86% yield,⁶² which are difficult to separate. Spiro[cyclopropane-1,4'-isoxazolidines] **83a–c** are more thermally stable than their regioisomers **82a–c**. The latter undergo rearrangement (400 °C, 0.2 mm Hg) to derivatives of 4-piperidones **84a–c** and enaminones, which allows one to isolate the isoxazolidines **83a–c** from the reaction mixture.



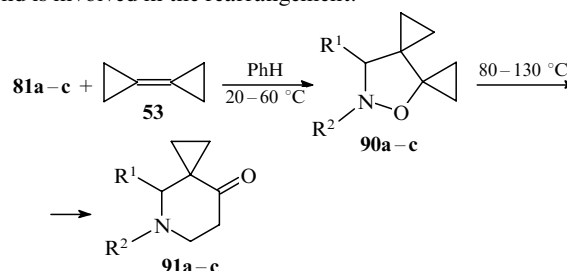
$\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$ (a); $\text{R}^1 - \text{R}^2 = \text{CH}_2\text{CH}_2\text{C}(\text{Me})_2$ (b), $(\text{CH}_2)_4$ (c).

The use of alkyl- and aryl-substituted methylenecyclopropanes and derivatives of cyclopropylidenecetic acid in these transformations makes it possible to obtain various fused spiro[cyclopropaneisoxazolidines] which are of interest as starting compounds in the syntheses of isoquinoline, quinolizidine, indolizidine and some other heterocyclic structures.^{63–72} Electron-donating substituents at the double bond favour the formation of spiro[cyclopropane-1,4'-isoxazolidines], whereas the 1,5'-regioisomers are formed in the presence of electron-withdrawing substituents. For example, the addition of cyclic nitrone **81b** to substituted methylenecyclopropane **85** results exclusively in isoxazolidine **86**, whereas the reaction of the same nitrone **81b** with the methyl ester **87a** or cyclopropylidenecetonitrile (**87b**) affords stereoisomeric spiro[cyclopropane-1,5'-isoxazolidines] **88a,b** and **89a,b**.^{63, 72}



Compound	R	Yield of 88 (%)	Yield of 89 (%)
a	CO ₂ Me	21	42
b	CN	70	17

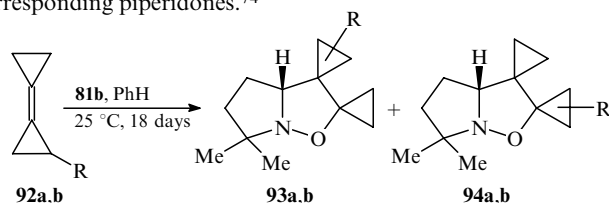
The nitrones **81a–c** react with bicyclopopylidene (**53**) at 20–60 °C to give high yields of isoxazolidines **90a–c**, in which both spirocyclopropane fragments are retained. However, heating of the reaction mixture in aromatic hydrocarbons as solvents at 80–130 °C results in isomerisation of the isoxazolidines obtained to the corresponding spiro[cyclopropane-1,3'-piperidin]-4-ones **91a–c**; only the cyclopropane ring adjacent to the labile N–O bond is involved in the rearrangement.^{73, 74}



Compound	R ¹	R ²	Yield of 90 (%)	Yield of 91 (%)
a	Ph	Me	93	63
b	(CH ₂) ₂ CMe ₂		80	80
c	(CH ₂) ₄		60	65

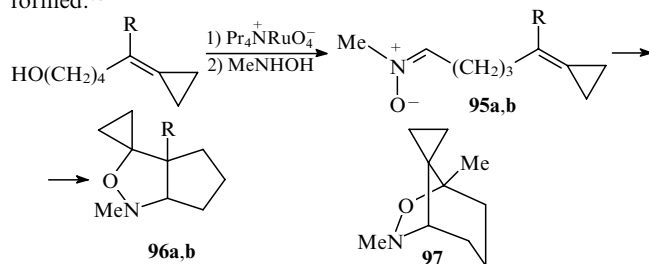
Isomerisation of isoxazolidines **90a–c** to piperidones **91a–c** probably occurs by homolytic cleavage of the N–O bond in the heterocycle followed by fast rearrangement of the radicals and ring closure.

Only reactions with nitrones with symmetrically substituted bicyclopopylidenes, where isoxazolidines incorporating a spirocyclopropane fragment are formed selectively, are of preparative value. Otherwise, a complex mixture of isomeric compounds is formed, as is the case, *e.g.*, of the cycloaddition of the nitrone **81b** to monosubstituted bicyclopopylidenes **92a,b**. Mixtures of isomers **93** and **94** (overall yield 65%–85%) could not be separated chromatographically or after their thermal rearrangement to the corresponding piperidones.⁷⁴



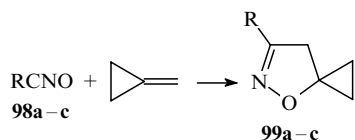
R = CO₂Me (**a**), SPH (**b**).

The cycloaddition of nitrones to the double bond of the methylenecyclopropane fragment can occur in an intramolecular manner as well. The reaction with nitrone **95a** containing a trisubstituted double bond (25 °C, 24 h, yield 87%) occurs regioselectively to give the cycloadduct **96a**. The presence of an additional methyl group in the nitrone **95b** decreases the polarity of the double bond and the reactivity of the nitrone. At 80 °C (2 h), a mixture of two isomers **96b** and **97** in the ratio ~ 2 : 1 is formed.⁷⁵

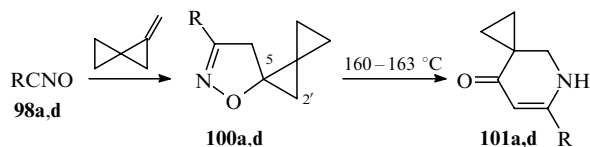


R = H (**a**), Me (**b**).

Unsaturated analogues of isoxazolidines, *viz.*, spiro[cyclopropanedihydroisoxazoles], can be obtained by 1,3-dipolar cycloaddition of nitrile oxides to methylenecyclopropanes. The reaction of nitrile oxides **98a–c** with non-substituted methylenecyclopropane occurs regioselectively to give spiro[cyclopropane-1,5'-dihydroisoxazoles] **99a–c**.⁷⁶ Only in the case of acetonitrile oxide (**98c**) was the formation of a different regioisomer (~ 3%) observed.



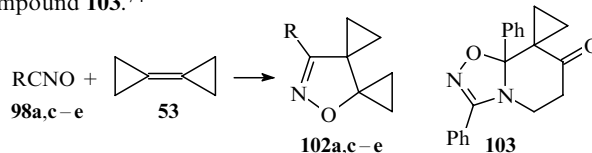
R = Ph (**a**, 65%), Bn (**b**, 35%), Me (**c**, 60%).



R = Ph (**100a**, 64%), 2,4,6-Me₃C₆H₂ (**100d**, 100%).

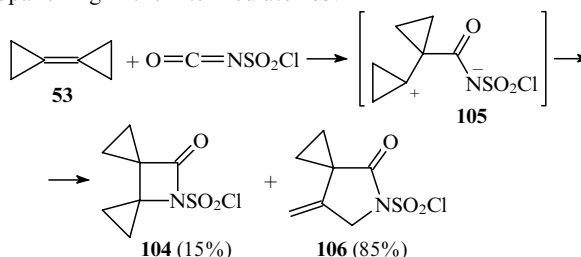
Spiro[cyclopropane-1,5'-dihydroisoxazoles] substituted in the cyclopropane ring are obtained in a similar way from nitrile oxides **98a–d** and substituted methylenecyclopropanes.⁷⁷ Reactions of methylenespiropentane with nitrile oxides **98a** (20 °C, 16 h) and **98d** (60 °C, 4 h) in benzene results in dihydroisoxazoles **100a,d**, thermal rearrangement of which to ketones **101a,d** occurs regioselectively, exclusively with opening of the inner cyclopropane ring at the C(5)–C(2') bond.⁷⁸

The cycloaddition of nitrile oxides **98a–c** to bicyclopopylidene (**53**) occurs less efficiently than to methylenecyclopropane.^{73,74} Because of this, partial dimerisation of nitrile oxides to furoxans occurs. The yields of dispirano dihydroisoxazoles **102** can be increased by performing slow generation of nitrile oxide *in situ* (*e.g.*, in the synthesis of nitrile oxide **98a** by treatment of benzohydroxymoyl chloride with NaHCO₃) or by using spatially hindered nitrile oxides, *e.g.*, **98d**. However, the presence of extremely bulky substituents in the nitrile oxide molecule, *e.g.*, in compound **98e**, again decreases the yield of the target product. It should be noted that in the case of the nitrile oxide **98a** the resulting dihydroisoxazole **102a** partially reacts with it to give compound **103**.⁷⁴

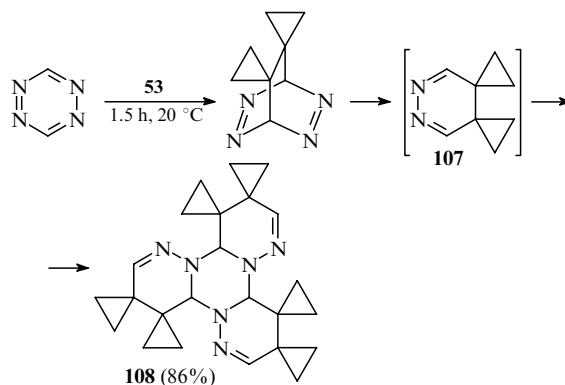


Compound	R	T / °C	t / days	Yield of 102 (%)
a	Ph	66	7	40
c	Me	20	7	10
d	2,4,6-Me ₃ C ₆ H ₂	110	2	67
e	Ph ₃ C	110	7	17

Bicyclopopylidene (**53**) undergoes [2 + 2]-cycloaddition to chlorosulfonyl isocyanate to give the β-lactam **104**, but this is not the main product. Evidently, the reaction can occur as a two-step process to give the 1,4-zwitter ion **105**. The main reaction product is methylenecyclopropane-γ-lactam **106** formed by opening of one cyclopropane ring in the intermediate **105**.⁵⁴

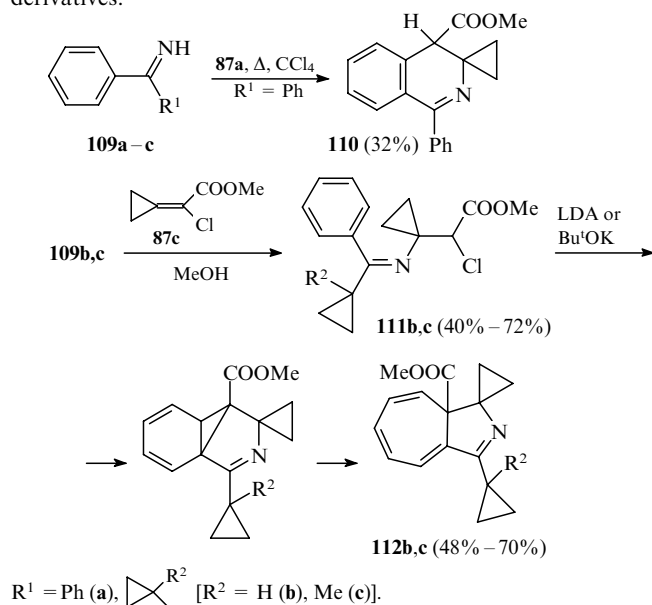


Bicyclopopylidene (**53**) readily undergoes [4 + 2]-cycloaddition to heterodienes such as 1,2,4,5-tetrazine and its derivatives. The primary cycloaddition product readily undergoes dedinitrogenation, while the resulting 8,9-diazadispiro[2.0.2.4]deca-7,9-diene (**107**) undergoes trimerisation to the fused heterocyclic

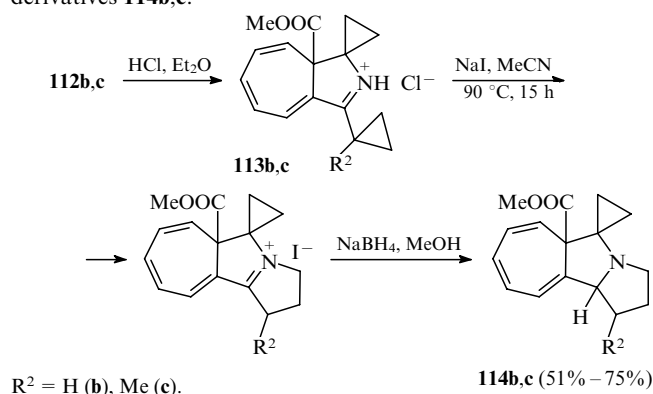


compound **108** with six spiro-fused cyclopropane fragments in the molecule (a mixture of two stereoisomers).⁷⁹ Attempts to trap the heterodiene **107** failed.

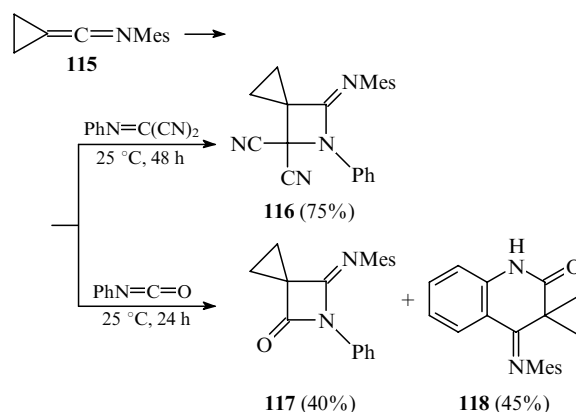
Synthesis of fused azaheterocycles with a spirocyclopropane fragment can be carried out by the reactions of cyclopropylideneacetates with imines. For example, the ester **87a** undergoes formal [4 + 2]-cycloaddition to imine **109a** to give spiro[cyclopropane-1,3'-dihydroisoquinoline] **110**. The reaction of chloro-substituted methylenecyclopropane **87c** with imines **109b,c** in methanol gives the Michael adducts **111b,c** in almost quantitative yields. These adducts are thermally stable, but in the presence of lithium diisopropylamide or potassium *tert*-butoxide, carbenes are generated; the latter are transformed to compounds **112b,c** with a dihydro-2-azaazulene skeleton due to intramolecular cycloaddition to the benzene ring followed by isomerisation.^{80,81} This bicyclic system has been studied much less than the 1-azaazulene derivatives.



The cyclopropyl substituent at position 1 of azaazulenes **112b,c** can be opened on treatment with electrophilic reagents, which enables intramolecular cyclisation of the salts **113b,c** to give derivatives **114b,c**.⁸¹

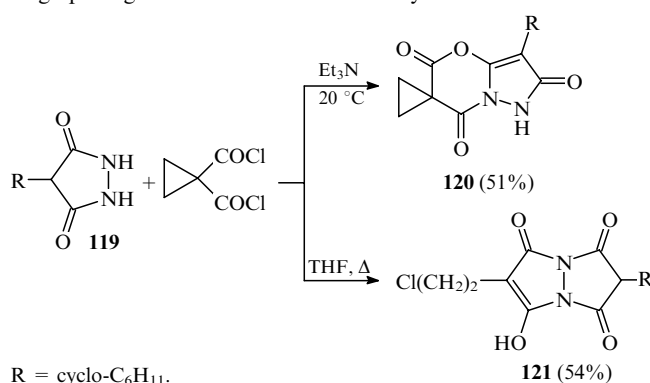


Unlike 1-alkenylidenecyclopropanes which react with dihydrotriazolodione **69** or with chlorosulfonyl isocyanate with opening of the cyclopropane ring,⁸² *N*-mesitylcyclopropylideneazomethine (**115**) reacts with *N*-(dicyanomethylidene)aniline or phenyl isocyanate to give spiro[azetidinecyclopropanes] **116** and **117**. In the latter case, a considerable amount of the cycloadduct **118** is formed.⁸³

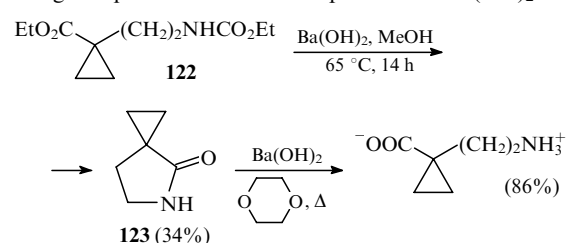


4. Other methods for the synthesis of azaheterocycles incorporating a spirocyclopropane fragment

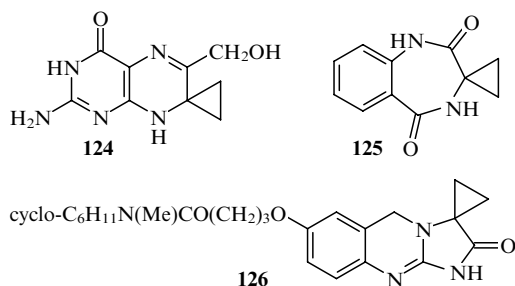
Heterocyclic compounds incorporating a spirocyclopropane fragment in the molecule can be obtained by typical cyclocondensations involving cyclopropane derivatives. However, certain conditions have to be observed in order to keep the cyclopropane fragment unchanged in the course of the reaction. For example, the reaction of pyrazolidine-3,5-dione **119** with 1,1-cyclopropanedicarbonyl dichloride in the presence of an equimolar amount of triethylamine results in compound **120** containing a three-carbon ring. On the other hand, this reaction carried out with heating in THF in the absence of a base is accompanied by the three-carbon ring opening and results in the chloroethyl derivative **121**.⁸⁴



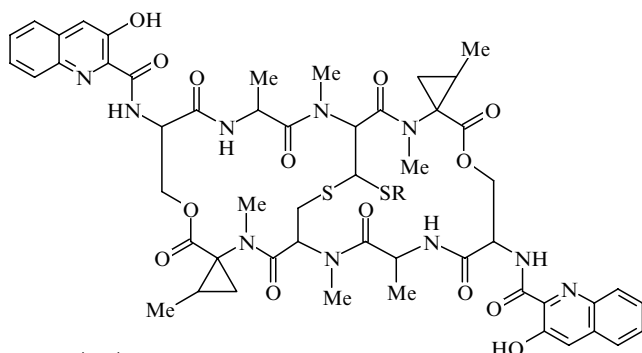
Intramolecular cyclisation of 1,1-disubstituted cyclopropane **122** on treatment with $\text{Ba}(\text{OH})_2$ results in lactam **123** containing a spirocyclopropane fragment. The latter undergoes heterocycle opening to give 1-(2-aminoethyl)cyclopropanecarboxylic acid on refluxing in aqueous dioxane in the presence of $\text{Ba}(\text{OH})_2$.⁸⁵



The cyclocondensation method with the use of 1-aminocyclopropanecarboxylic acid or its derivatives as structural blocks was used for a directed synthesis of a series of spiro compounds, *e.g.* **124**–**126**, which may be interesting as potential medicines.^{86–88} For example, benzodiazepine **125** was obtained in 48% yield by cyclocondensation of methyl 1-aminocyclopropanecarboxylate with *o*-nitrobenzaldehyde.⁸⁸

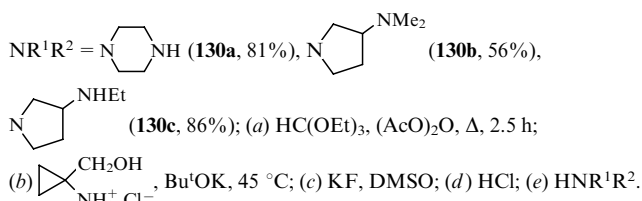
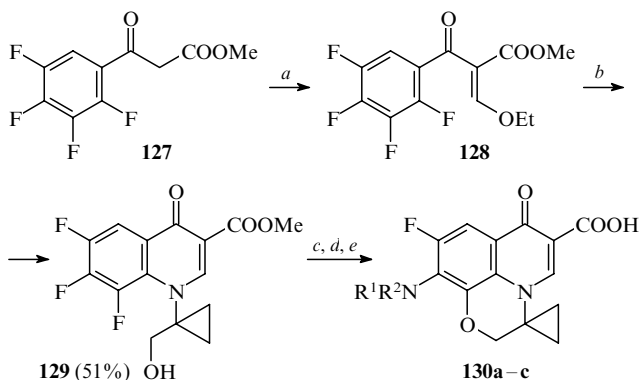


The 1-methylamino-2-methylcyclopropanecarboxylic acid moiety spiro-fused with the macrocycle is a constituent of cyclic octadepsipeptides, which are bifunctional antibiotics of the quinomycin series that can be intercalated into DNA.^{89, 90}



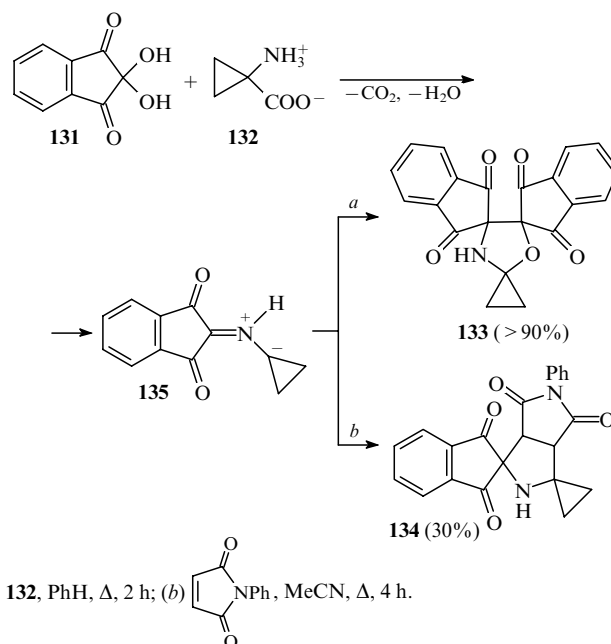
R = Buⁱ, Prⁱ, Me.

The incorporation of the spirocyclopropane fragment in the benzoxazine heterocycle of ofloxacin (a well-known antibacterial compound belonging to the fluoroquinolone series) was carried out according to the following scheme: condensation of β -oxoester **127** with triethyl orthoformate to give unsaturated ester **128**; formation of the 1,4-oxazine ring containing a spirocyclopropane fragment by treating compound **128** with 1-(hydroxymethyl)cyclopropylamine hydrochloride followed by heating of the reaction product **129** with anhydrous potassium fluoride in DMSO. Acid hydrolysis of the ester group followed by selective replacement of a fluorine atom by cyclic amines afforded the target compounds **130**.⁹¹



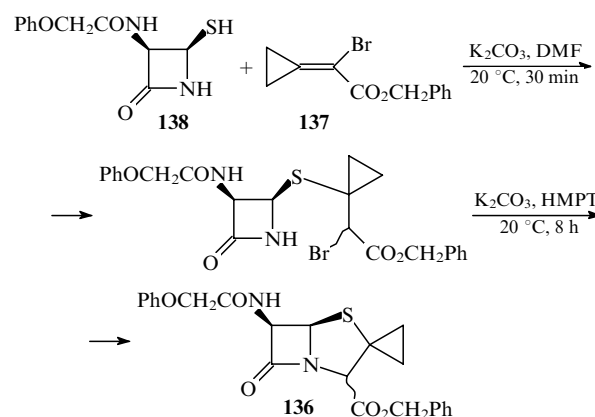
In the reaction of ninhydrin (indan-1,2,3-trione hydrate) (**131**) with 1-aminocyclopropanecarboxylic acid (**132**) (molar ratio 1 : 2) in boiling benzene, decarboxylation of the acid **132** occurs to give spiro[cyclopropane-1,5'-pyrrolidine] **133**. The reaction of equimolar amounts of the acid **132**, ninhydrin (**131**) and *N*-phenyl-

maleimide in acetonitrile under reflux results in spiro[cyclopropane-1,5'-pyrrolidine] **134**.⁹² It is assumed⁹² that these reactions involve the intermediate 1,3-dipole **135**.



In certain cases, the corresponding cyclopropane derivatives were deliberately obtained for the directed syntheses of biologically active compounds containing a spirocyclopropane fragment. For example, (1-benzyloxycarbonyl-1-bromomethylidene)cyclopropane (**137**) was obtained for the synthesis of the cyclopropane analogue of norpenicillin **136**.⁹³ The reaction of compound **137** with 4-mercaptoazetidin-2-one **138** in the presence of K₂CO₃ results in epimeric 2-bisnorpenicillanates **136** (ratio ~ 4 : 1, yield ~ 25%).⁹⁴

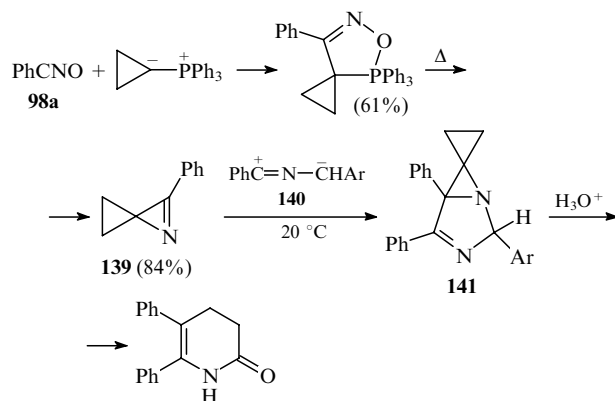
Although the yields of the adducts are low, this method is considered to be convenient⁹⁴ because it does not give rise to side transformations of the cyclopropane ring.



HMPT is hexamethylphosphorous triamide.

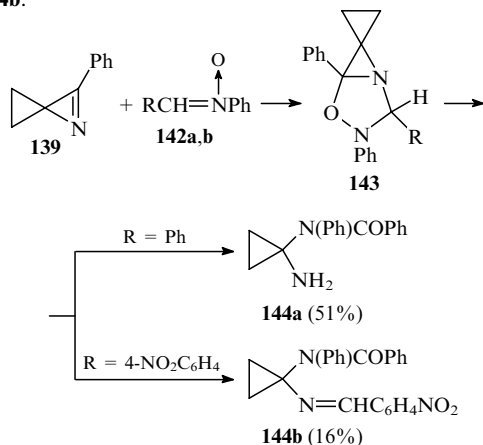
It is well known⁹⁵ that 1-azirines are widely used in the synthesis of heterocyclic systems containing a nitrogen atom in the ring. Highly strained 2-phenyl-1-azaspiropent-1-ene (**139**) is a useful starting compound for the synthesis of azaheterocycles containing a spirocyclopropane fragment. This compound is obtained by pyrolysis of the addition product of benzonitrile oxide **98a** to cyclopropylidenephosphorane.⁹⁶ The reaction of the spirane **139** with benzonitrile-4-nitrobenzylidene (**140**) generated *in situ* from *N*-(4-nitrobenzyl)benzimidoyl chloride occurs regioselectively to give the spiro{cyclopropane-1,6'-1,3-diazabicyclo[3.1.0]hex-3-ene} derivative **141**, the structure of which was

established from spectroscopic data and by its hydrolysis into 3,4-dihydro-5,6-diphenyl-2-pyridone.⁹⁷



Ar = 4-NO₂C₆H₄.

It is well known⁹⁸ that nitrones undergo 1,3-dipolar cycloaddition to compounds containing C=N bonds. Aziridine **139** also reacts with nitrones **142a,b**; however, the resulting cycloadducts **143a,b** are unstable under the reaction conditions (benzene, Δ) and are transformed into cyclopropylamides **144a** or **144b**.⁹⁷



R = Ph (a), 4-NO₂C₆H₄ (b).

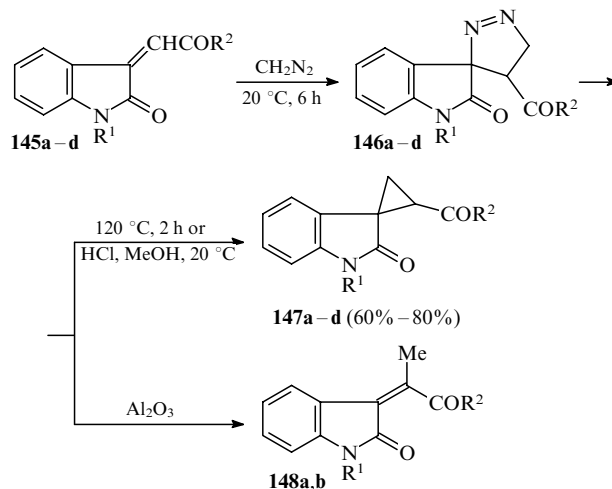
III. Formation of a cyclopropane ring spiro-fused with a heterocycle

Cycloaddition of various reagents to methyldene derivatives of the corresponding heterocycles is one of the general ways to form a spiro-fused cyclopropane ring in heterocyclic compounds. Cyclopropanation of the double bond, which is usually activated by electron-withdrawing substituents, is mostly carried out by reactions with diazo compounds and ylides. In some cases, an opposite approach is used, where the required azaheterocycle contains a diazo group capable of reacting with an unsaturated substrate. In any case, the originally formed dihydropyrazoles, *i.e.*, 1,3-dipolar cycloadducts, are then transformed into cyclopropane derivatives upon elimination of a nitrogen molecule; depending on the nature of the substituents, this either occurs spontaneously at room temperature or requires elevated temperatures. In a number of cases, the choice of the target heterocyclic compounds, *e.g.*, indolinones or cephalosporins, is dictated by the search for new biologically active compounds.^{99–104}

1. Construction of a cyclopropane ring based on the formation and dedinitrogenation of dihydropyrazoles

The addition of diazomethane to methyldeneindolin-2-one derivatives **145a–d** results in spiro[indoline-3,3'-dihydropyrazoles] **146a–d** with high regioselectivity.^{102,103} Their thermolysis in boiling dioxane or treatment with HCl in MeOH at room temper-

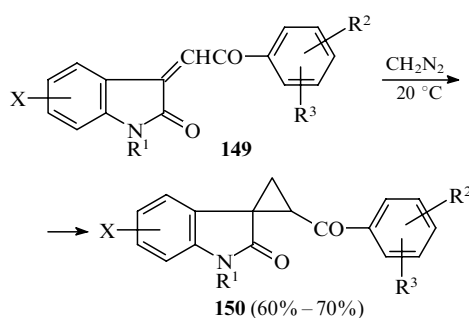
ature involves elimination of nitrogen to give spiro[cyclopropane-1,3'-indolin]-2-ones **147a–d**. Chromatography of dihydropyrazoles **146a,b** on Al₂O₃ is accompanied by their transformation to conjugated enones **148a,b** (yields 57% and 74%, respectively) rather than to compounds **147a,b**.¹⁰³



R¹ = H, R² = Ph (**146a**, 92%), Me (**146b**, 90%), OEt (**146c**, 62%);

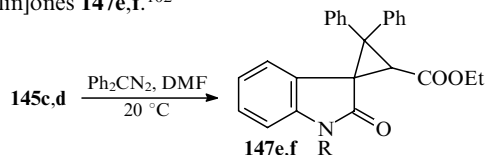
R¹ = CH₂N(CH₂)₂O, R² = OEt (**146d**, 74%).

Unlike methyldeneindolin-2-ones **145a–d**, fluoro-substituted 3-(arylmethyldene)indolin-2-ones **149** react with an ethereal solution of CH₂N₂ at 20 °C to give directly spiro[cyclopropaneindolin]ones **150**.¹⁰⁴



X = H, 5-F, 6-F; R¹ = H, COMe, CH₂N(CH₂)₂O; R² = 2-F, 4-F; R³ = H, 2-Me, 3-Me, 5-Me, 3-Cl, 3-F.

As in the example considered above, 1,3-dipolar cycloaddition of diphenyldiazomethane to methyldeneindolin-2-ones **145c,d** in DMF at 20 °C involves nitrogen elimination from the dihydropyrazoles formed originally to give spiro[cyclopropaneindolin]ones **147e,f**.¹⁰²

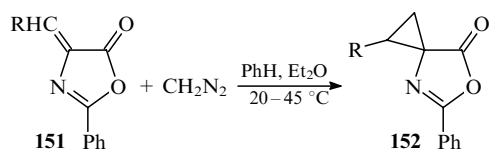


R = H (**147e**, 53%), CH₂N(CH₂)₂O (**147f**, 76%).

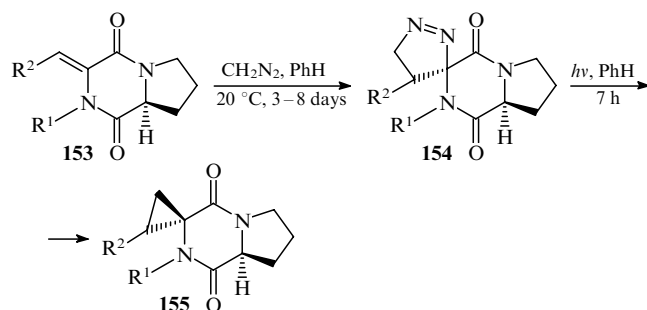
A similar approach to the construction of a spiro-fused cyclopropane fragment is also applicable to other heterocyclic systems; depending on the nature of the azaheterocycle and the substituents in the ring, the reaction of diazo compounds with the exocyclic double bond can involve both the formation of the intermediate dihydropyrazoles and their spontaneous dedinitrogenation.

The methods (including enantioselective ones) for the synthesis of 1-aminocyclopropanecarboxylic acid derivatives were

developed using 1,3-dipolar cycloaddition of diazomethane to 4-alkylidene(arylidene)-5(4*H*)oxazolones,^{105–108} thiazolones¹⁰⁹ and piperazinediones.^{110–112} The reaction with oxazolones **151** occurs at 20–45 °C with nitrogen elimination and formation of spiro[cyclopropanoxazolines] **152**. On the other hand, the reaction of CH₂N₂ with piperazinediones **153a,b** gives spiro-fused azaheterocycles **154** in high yields and with high diastereoselectivity (> 95%). Photolysis of the latter results in azaheterocycles **155** in > 90% yields. Acid splitting of the six-membered heterocycle in the resulting compounds on treatment with 6*M* HCl in AcOH at 100 °C results in 1-aminocyclopropanecarboxylic acid derivatives.^{110, 111}

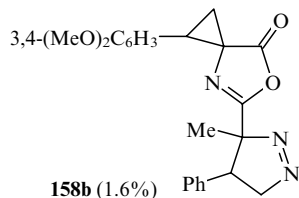
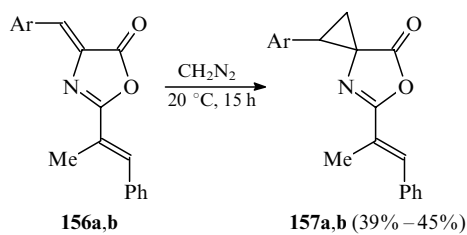


R = Ph, 4-ClC₆H₄, 4-MeC₆H₄, 4-MeOC₆H₄ (45%–60%), Me (25%), Cl (75%), Br.



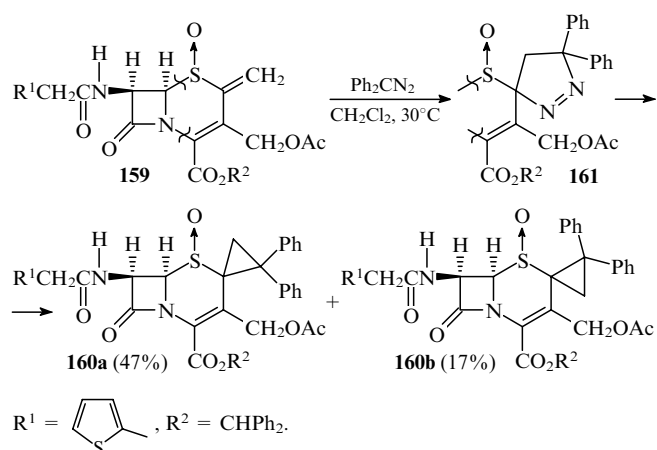
R¹ = Ac, R² = Ph (**a**); R¹ = Bu^tOCO (Boc), R² = Et (**b**).

If the oxazolone ring contains both substituted methylidene and vinyl fragments (*cf.* compounds **156a,b**), the addition of diazomethane occurs mainly to the methylidene fragment and the corresponding cyclopropane derivatives **157a,b** are formed as the reaction products even at room temperature.¹¹³ The addition of diazomethane to the vinyl group occurs only in compound **156b** and only to a minor extent to give the dihydropyrazole **158b**, which is stable under these conditions.

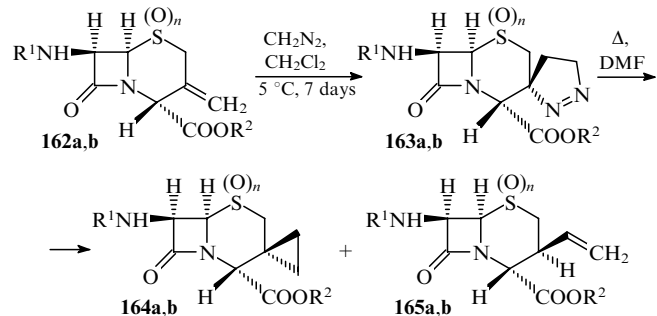


Ar = Ph (**a**), 3,4-(MeO)₂C₆H₃ (**b**).

The formation of a cyclopropane fragment spiro-fused with the heterocyclic system of cephalosporins is documented.¹¹⁴ For example, diphenyldiazomethane adds to the exocyclic double bond of 2-methylidenecephemes **159** (30 °C, 30 min) to give two isomeric spiro derivatives **160a** and **160b** in the ratio ~ 3 : 1. It is believed¹¹⁴ that the reaction occurs through regioselective formation of the dihydropyrazole **161**.



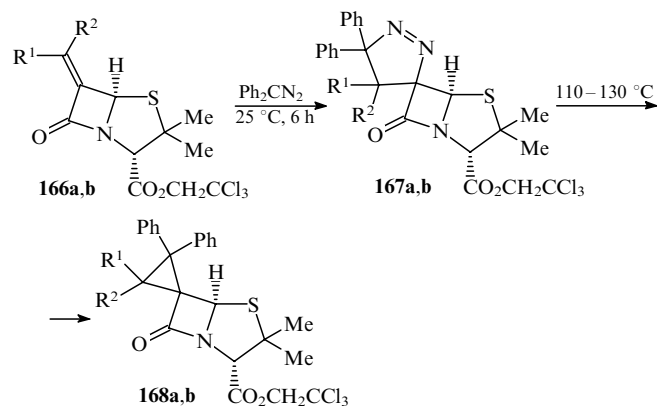
1,3-Dipolar cycloaddition of diazomethane to 3-methylidenecephemes **162** occurs at 5 °C in 1 week and only with a great excess of diazomethane.¹¹⁵ 1,3-Dipolar cycloaddition products **163** containing a spiro-fused dihydropyrazole fragment is formed in the first stage.



n = 0 (**a**), 1 (**b**); R¹ = PhOCH₂CO; R² = 4-NO₂C₆H₄CH₂.

Subsequent thermolysis of the resulting 1-dihydropyrazoles **163a,b** occurs non-selectively and results in both products with a cyclopropane fragment, *i.e.*, spiro[cephame-1,3'-cyclopropanes] **164a,b** (yields 60% and 64%, respectively), and their isomers, *i.e.*, 3-vinylcephemes **165a,b** (20% and 15% yields, respectively).¹¹⁵

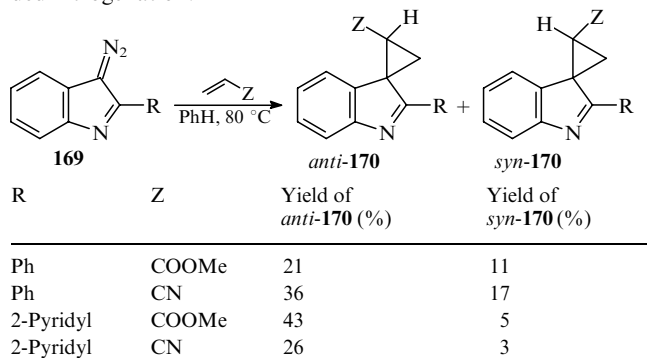
Pure *E*- and *Z*-isomers of 2,2,2-trichloroethyl penicillanates **166** containing an exocyclic double bond react with diphenyldiazomethane to give stable 4,5-dihydro-3*H*-pyrazoles **167a** or **167b**, pyrolysis of which occurs stereospecifically and results in penicillanates **168** with a spirocyclopropane fragment.¹¹⁶



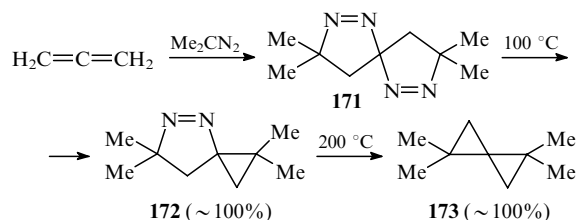
Compound	R ¹	R ²	Yield of 167 (%)	Yield of 168 (%)
a	CO ₂ Bn	H	72	89
b	H	CO ₂ Bn	87	15

The cyclopropane fragment spiro-fused with a heterocycle also results from the addition of the corresponding diazo hetero-

cycles to activated alkenes followed by dedinitrogenation of the resulting dihydropyrazole. For example, the reaction of 3-diazoindoles **169** with methyl acrylate or acrylonitrile in boiling benzene results in nitrogen elimination to give substituted spiro[cyclopropane-1,3'-indoles] **170** with the preferential formation of *anti*-isomers.¹¹⁷ It should be noted that diazo compounds **169** are rather stable under the same conditions in the absence of unsaturated substrates. It is therefore assumed that their reactions with methyl acrylate and acrylonitrile occur as 1,3-dipolar cycloaddition; the intermediate dihydropyrazoles undergo spontaneous dedinitrogenation.



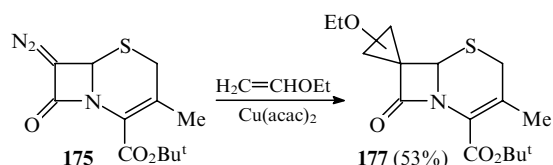
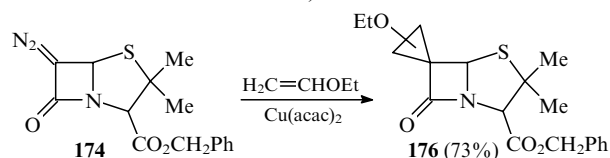
Exhaustive 1,3-dipolar cycloaddition of aliphatic diazo compound to allenes followed by partial dedinitrogenation of the resulting spiro-fused bis(dihydropyrazoles) makes it possible to form fragments of an azaheterocycle and a spirocyclopropane simultaneously.^{118,119} For example, bis(dihydropyrazole) **171** synthesised by the addition of 2-diazopropane to allene is transformed into spiro[cyclopropanedihydropyrazole] **172** on heating to 100 °C. The loss of the second nitrogen molecule to give tetramethylspiropentane (**173**) occurs only at 200 °C.¹¹⁸



2. Cyclopropanation of unsaturated compounds with sulfur carbenes and sulfur ylides

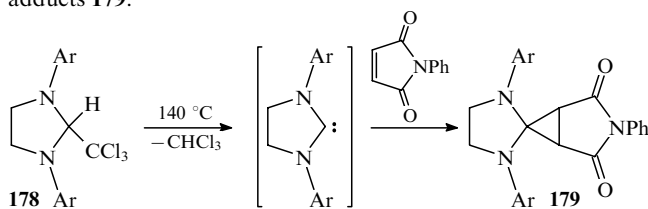
Although the cyclopropanation of unsaturated compounds with carbenes and their synthetic equivalents is a popular modern method for the construction of three-carbon rings, there are but a few examples of such reactions resulting in azaheterocycles fused with a spirocyclopropane fragment.

Cyclopropanation of alkenes with heterocyclic diazo compounds in the presence of catalysts is an example. Diazopenicillanates and diazocephemes have been reported as cyclopropanating reagents.¹¹⁶ This method is an alternative to the reaction of aliphatic diazo compounds with methylenepenicillanates or methylenecephemes in the construction of the same structural fragments. Cyclopropanation of unsaturated compounds activated by electron-donating substituents occurs successfully. For example, the reaction of benzyl 6-diazopenicillanate (**174**) or 7-diazoceph-3-ene (**175**) with ethyl vinyl ether in the presence of copper acetylacetonate results in ethoxycyclopropanes **176** or **177** (each as a mixture of four isomers).¹²⁰



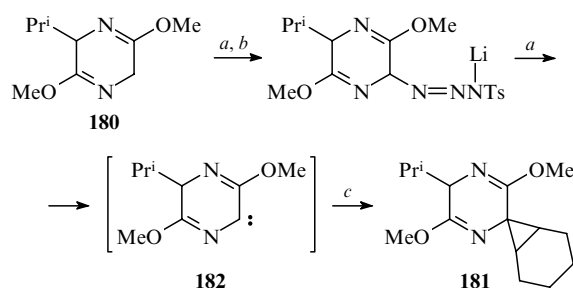
The reaction of diazo compounds **174** and **175** with vinyl acetate in the presence of Cu(acac)₂ occurs similarly, but the yields of the products do not exceed 10% due to the low stability of the resulting spiro-fused acetoxycyclopropanes.¹²⁰ The reaction of diazo compounds **174** and **175** with alkenes containing electron-withdrawing groups, both in the presence and in the absence of Cu(acac)₂, occurs as 1,3-dipolar cycloaddition and results only in the corresponding spiro-fused 4,5-dihydro-1*H*-pyrazoles.¹²⁰

Refluxing of trichloromethyl derivatives of imidazolidines **178** in xylene is presumably accompanied by the abstraction of CHCl₃ and generation of a nucleophilic heterocyclic carbene which can add to activated double bonds. For example, the reaction with *N*-phenylmaleimide affords spirocyclopropane-containing adducts **179**.¹²¹



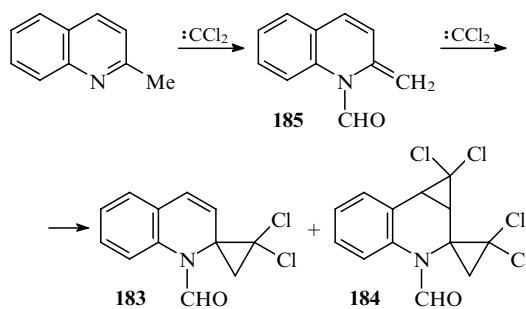
Ar = Ph (85%), 4-MeC₆H₄ (57%), 4-MeOC₆H₄ (77%).

The reaction of dihydropyrazine **180** with butyllithium and tosyl azide at –70 °C in the presence of cyclohexene results in the spirane adduct **181** (overall yield > 70% with respect to the starting dihydropyrazine **180**) due to generation and [1 + 2]-cycloaddition of the heterocyclic carbene **182**.¹²²



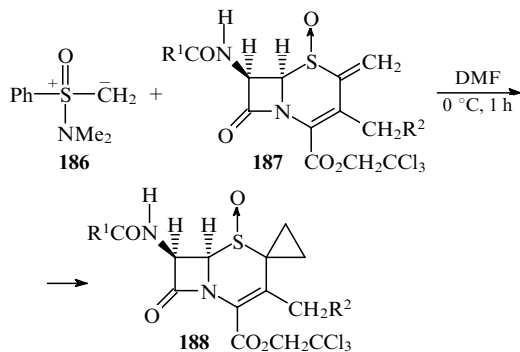
(a) BuLi; (b) TsN₃, –70 °C; (c)

Dichlorocyclopropanation of 2-methylquinoline at 25 °C (CHCl₃, 50% NaOH, Et₃N⁺ BnCl[–]) occurs in rather high yields to give compounds **183** and **184** with a spiro[cyclopropane-1,2'-quinoline] structure. Probably, dichlorocarbene first adds to the nitrogen atom to give an ylide, which generates 1-formyl-2-methylidenedihydroquinoline (**185**) in alkaline medium; the latter undergoes the usual dichlorocyclopropanation.¹²³

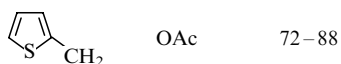


The method for building the cyclopropane ring by addition of reactive sulfur ylides to double bonds is commonly used in synthetic organic chemistry.¹²⁴ Unlike the reactions with electrophilic carbenes, alkenes activated with electron-withdrawing groups (Michael acceptors) are used in these processes.

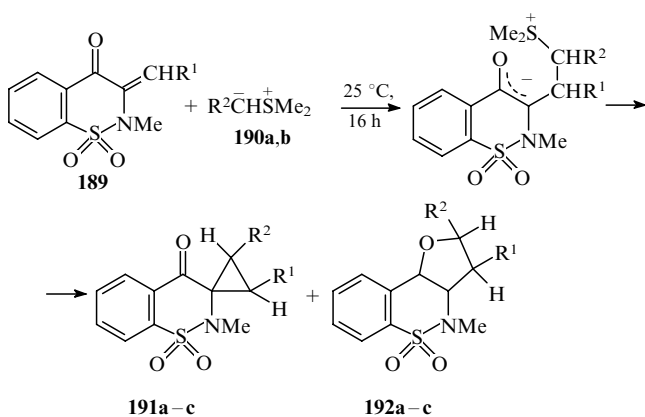
Back in 1973, Spry¹²⁵ demonstrated the possibility of using sulfur ylides for the cyclopropanation of 2-methylidenecephalosporins. For example, the reaction of sulfonylmethylide **186** with functionally substituted methylidenecephemes **187** occurs exclusively at the exocyclic double bond to give spiro[cephalosporin-cyclopropanes] **188** in high yields.¹²⁵



R ¹	R ²	Yield (%)
PhOCH ₂	H	80
PhOCH ₂	OAc	85
Me	OAc	64



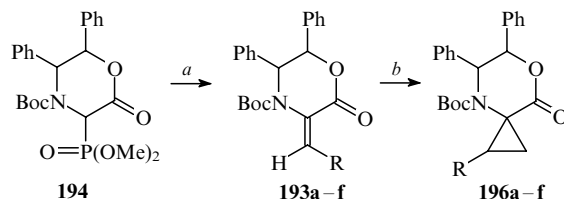
The reaction of 3-methylidene-2,3-dihydrothiazin-4-one derivatives **189** containing an enone system with ylides **190** results in spiro[cyclopropanedihydrothiazines] **191**.¹²⁶ If ylide **190** contains a benzoyl substituent, a mixture (~1:2) of spirocyclopropane and dihydrofuran derivatives **191b,c** and **192b,c** is formed. Unsaturated ylide **190** (R² = H) reacts with the enone **189** (R¹ = Ph) to give only spiro[cyclopropanedihydro-1,2-benzothiazine] **191a**. It is believed¹²⁶ that the process starts with nucleophilic attack of ylides **190** on the β-carbon atom of the C=C bond in the enones **189**; this results in resonance-stabilised betaines, which then undergo cyclisation at the carbon or oxygen atoms to give three- or five-membered rings. The direction of betaine cyclisation is determined by both electronic and steric factors.¹²⁶



R¹ = Ph, Me; R² = H, COPh.

Compound	R ¹	R ²	Yield of 191 (%)	Yield of 192 (%)
a	Ph	H	80	—
b	Me	COPh	22	52
c	Ph	COPh	24	55

A common method for the introduction of the spirocyclopropane fragment in a morpholinone structure is the reaction of their methylenes derivatives **193**, which are obtained from the phosphonate **194** using the Wittig reaction, with sulfur ylides.¹²⁷ It should be noted that the diastereoselectivity of methylenation of the double bond by the ylide **195** is higher than that by the ylide **190a**; diastereomers of spirane derivatives **196a-f** are formed preferentially (or exclusively) in yields higher than 82% (with the exception for compound **196e**). It should be noted that the addition of diazomethane to ethylenemorpholinone **193b** followed by photolysis of the resulting dihydropyrazole affords a diastereomeric mixture of spirane **196b** (ratio 1:1.6, overall yield 91%).¹²⁷



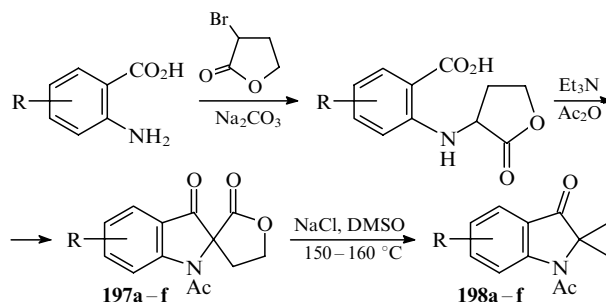
R = H (**a**), Me (**b**), Et (**c**), Prⁿ (**d**), Prⁱ (**e**), Ph (**f**);

(a) RCHO, NaH, THF; (b) PhS(O)(NEt₂)CH₂⁺ (**195**).

3. Decarboxylation and γ-elimination leading to cyclopropane ring formation

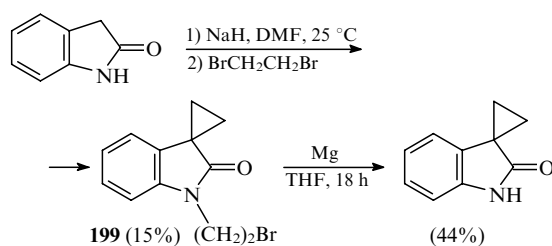
The formation of a spiro-fused cyclopropane fragment is carried out by decarboxylation of γ-lactones **197** spiro-fused with a heterocyclic system, besides elimination of an N₂ molecule from dihydropyrazoles. This method was used for the synthesis of spiro[cyclopropane-1,2'-indolin]-3-ones **198** with substituents both in the benzene ring and at the nitrogen atom aimed at the search for novel compounds with antiinflammatory and analgesic effects.^{99, 100, 128}

Spiro-fused γ-lactones **197a-f** are obtained in two steps by condensation of the corresponding anthranilic acids with α-bromo-γ-butyrolactone. Decarboxylation of the lactones **197a-f** is carried out by heating (150–160 °C) in the presence of an alkali metal chloride to give the heterocycles **198** in 75%–94% yields.^{100, 128} Functionalisation of the benzene ring in the spiro-lactone **197a** is carried out before the decarboxylation step.

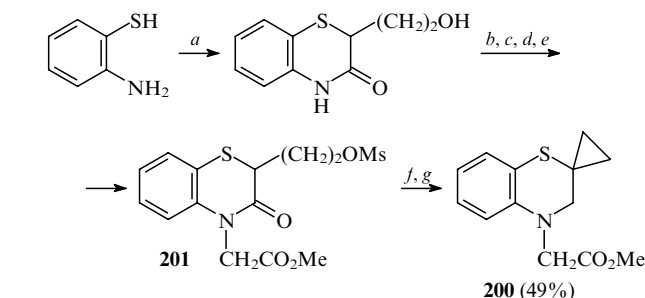


R = H (**a**), Me (**b**), OMe (**c**), Cl (**d**), Br (**e**), I (**f**).

1,3-Elimination from the corresponding functional derivatives is a useful method for the formation of a spiro-fused cyclopropane fragment applicable to various azaheterocyclic structures. In particular, this type of reaction includes cycloalkylation of compounds containing reactive hydrogen atoms with 1,2-dibromoethane. For example, the reaction of indolin-2-one with 2 equiv. of dibromoethane in the presence of sodium hydride results in compound **199**, subsequent reduction of which with magnesium in boiling THF gives unsaturated spiro[cyclopropane-1,3'-indolin]-2-one, which was later used for the synthesis of compounds with potential pharmacological activity.^{129, 130}

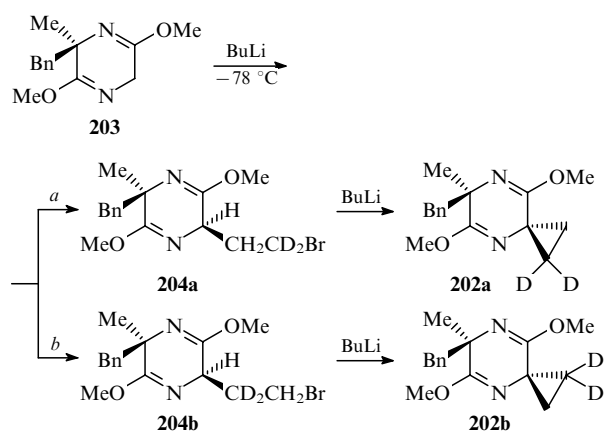


A scheme for the synthesis of spiro[1,4-benzothiazine]cyclopropan-3-one **200** with the use of 2-aminobenzethiol as the starting compound is presented below. The required functionalised ethyl group is introduced in the initial condensation step, while the spirocyclopropane fragment is formed in the last step, *i.e.*, cyclisation of mesylate **201**.¹³¹



(a) $\text{BrCH}_2\text{CH}_2\text{OH}$, K_2CO_3 , EtOH; (b) $\text{OCH}_2\text{CH}_2\text{OH}$, H^+ ; (c) $\text{BrCH}_2\text{CO}_2\text{Me}$; (d) MeOH, TsOH; (e) MsCl, Et₃N, CH₂Cl₂; (f) NaH, 20 °C, 30 min; (g) 70 °C, 15 min.

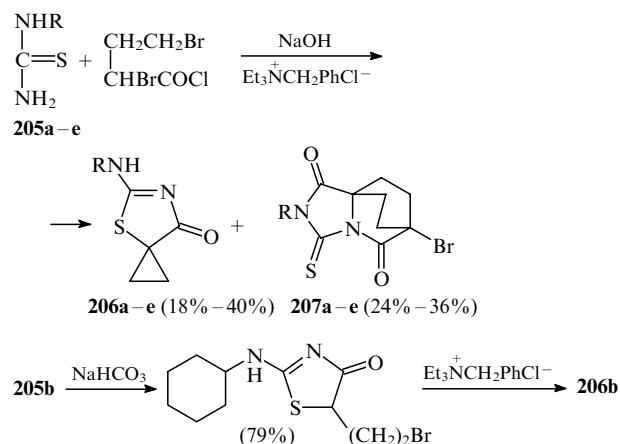
Alkylation followed by 1,3-elimination was successfully used for a stereoselective synthesis of (*R*)- and (*S*)-isomers of 1-amino-2,2-dideuteriocyclopropanecarboxylic acid. Spiranes **202** were used as the starting compounds which were then hydrolysed with HCl. These transformations could also be performed starting from chiral dihydropyrazine **203** and selectively deuterated 2-bromoethyl triflates.^{132, 133} Metallation of compounds **203** followed by alkylation with deuterated 2-bromoethyl triflate first gives (2-bromoethyl)dihydropyrazine **204a,b** (yield 86%–88%); in this case, an isomer with a *cis* arrangement of the benzyl and bromoethyl substituents is formed as the main product. Subsequent cyclisation of compounds **204a,b** on treatment with BuLi in THF affords spiro[cyclopropanedihydropyrazines] **202a,b** (yield 46%–55%).^{132, 133}



(a) $\text{BrCD}_2\text{CH}_2\text{OTf}$; (b) $\text{BrCH}_2\text{CD}_2\text{OTf}$.

In some cases, consecutive chemical transformations result in the formation of heterocyclic and then cyclopropane fragments. For example, the reaction of substituted thioureas **205a–e** with 2,4-dibromobutanoyl chloride occurs on treatment with 5% NaOH in the presence of benzytriethylammonium chloride

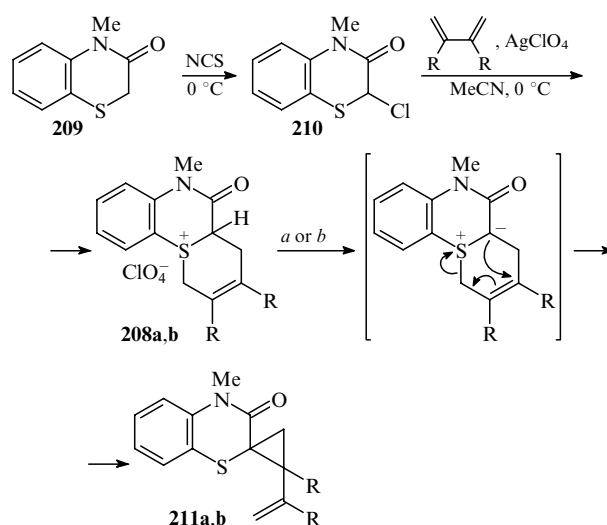
and results in a mixture of spiro[cyclopropane-1,5'-dihydrothiazol]-4-one derivatives **206a–e** (yields 18%–40%) and tricyclic compounds **207a–e**.¹³⁴ The reaction occurs in two steps, as shown for cyclohexylthiourea **205b**.



R = Bu (a), cyclo-C₆H₁₁ (b), Bn (c), Ph (d),  (e).

4. Miscellaneous methods for the formation of a spiro-fused cyclopropane fragment

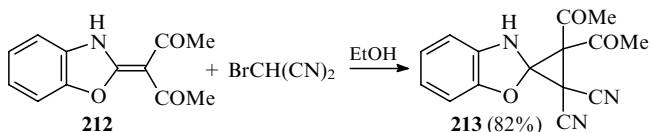
A particular case of the formation of a cyclopropane ring spiro-fused with a thiazine fragment is represented by the transformation of tricyclic benzothiazine salts **208a,b**, which are obtained by chlorination of benzothiazine **209** followed by treatment of the resulting α -chloro derivative **210** with 1,3-dienes in the presence of AgClO₄.¹³⁵ Treatment of the benzothiazinium salts **208a,b** with reducing agents or bases results in 2'-vinylspiro[cyclopropane-1,2'-thiazines] **211a,b** in 56%–90% yields. Electrolysis of the salt **208a** in acetonitrile (1 h) also results in spiro[cyclopropane-1,2'-thiazine] **211a** in ~60% yield. It was found by X-ray diffraction analysis that the vinyl group and the sulfur atom in compound **211a** are *syn*-arranged. It was assumed¹³⁵ that the formation of spiro[cyclopropane-1,2'-thiazines] **211a,b** can follow both an ionic and a radical mechanism, although it was not specified which particular intermediates of radical nature can be generated in this system.¹³⁵



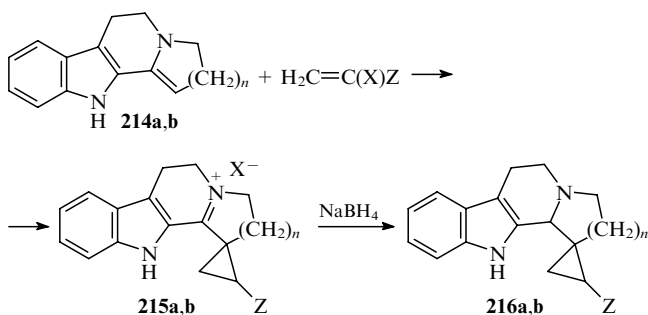
R = Me (a), H (b); (a) 20 °C: Mg, THF, or NaBH₄, EtOH, or Zn, AcOH; (b) B[–].

A spirocyclopropane fragment is formed in the reaction of bromomalonodinitrile with the electron-deficient exocyclic double bond of 2-methylidene-substituted dihydrobenzoxazole **212**.

Spiro[cyclopropane-1,2'-dihydrobenzoxazole] **213** is formed when an equimolar mixture of the reactants is kept for 2 h at 25 °C in 95% ethanol in the absence of bases.¹³⁶

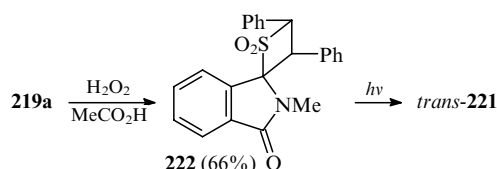
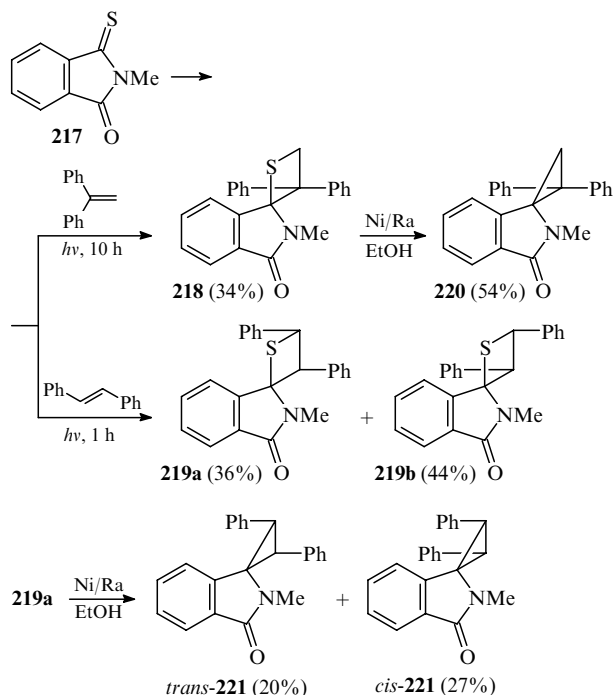


The reaction of polycyclic enamines **214** with methyl 1-bromoacrylate or 1-chloroacrylonitrile results in spirocyclopropane-containing hexahydroindolindolizine (**215a**) or hexahydroindolindolizine (**215b**) salts. Treatment of these salts with NaBH₄ or other reducing agents results either in compounds **216** containing a spirocyclopropane fragment (in moderate yields) or in deeper reduction with the cyclopropane ring opening.^{137, 138}



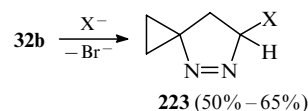
$n = 1$ (**a**), 2 (**b**); $X = \text{Cl}, \text{Br}$; $Z = \text{COOMe}, \text{CN}$.

Desulfurisation of thietane derivatives can serve as yet another method for the formation of a cyclopropane fragment spiro-fused with an azaheterocycle. In particular, photolysis of a mixture of *N*-methylmonothiophthalimide (**217**) with 1,1-diphenylethylene or *trans*-stilbene results in spiro-fused thietanes **218** or **219a,b**,¹³⁹ desulfurisation of which with Raney nickel (Ni/Ra) in ethanol affords spiro[cyclopropane-1,3'-isindolin]-1-ones **220** and **221**; a mixture of two isomeric compounds, viz., *trans*- and *cis*-**221**, is formed from the isomer **219a** under these conditions. However, only one derivative, viz., *trans*-**221**, is obtained in almost quantitative yield if thietane **219a** is first oxidised with hydrogen peroxide in acetic acid to give sulfone **222**, which is then subject to photolysis.¹³⁹



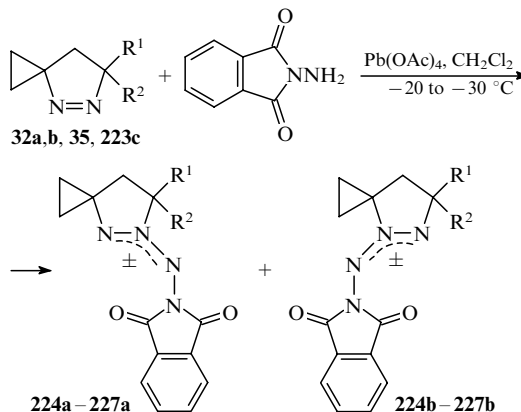
IV. Functionalisation of heterocyclic compounds containing a spirocyclopropane fragment

In this Section, we consider chemical transformations of aza-heterocycles containing a spirocyclopropane fragment, which is preserved in these reactions. In particular, chemical modifications of 5-bromospiro[cyclopropane-1,3'-4,5-dihydro-3*H*-pyrazole] (**32b**) and 3-*R*-spiro[cyclopropane-1,5'-4,5-dihydro-1*H*-pyrazoles] **36a,b**, which have recently become accessible (see Section II), were studied.^{33, 36} It was found^{33, 140} that the bromine atom in compound **32b** can be replaced by nucleophiles such as PhO, PhS or N₃ to give compounds **223**, in which the spiro[cyclopropane-1,5'-dihydropyrazole] structure remains intact.



$X = \text{OPh}$ (**a**), SPh (**b**), N_3 (**c**).

It was shown recently^{32, 140} that 4,5-dihydro-3*H*-pyrazoles **32a,b**, **35** and **223c** add phthalimidonitrene, which is obtained *in situ* upon oxidation of *N*-aminophthalimide with Pb(OAc)₄, to give pyrazolinio-*N*-phthalimidoamides (azimines) **224a,b**–**227a,b** with retention of the cyclopropane ring. In this case, the regioisomers **a** are formed preferentially from all 4,5-dihydro-3*H*-pyrazoles (or exclusively from ester **35**).

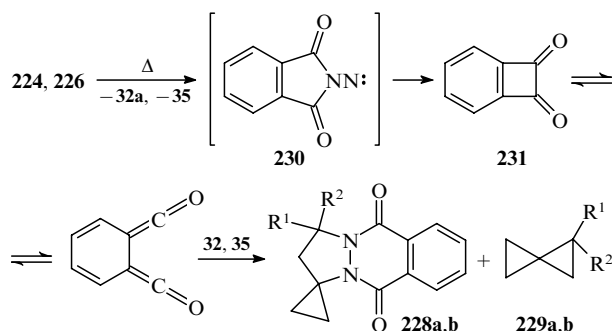


Compound	R ¹	R ²	Yield (%)	Ratio a : b
224	H	Ph	70–75	5.5 : 1
225	H	Br	30–35	see ^a
226	Me	COOMe	50–55	1 : 0
227	H	N ₃	60–65	3.3 : 1

^a The isomer **225b** is unstable under the reaction conditions.

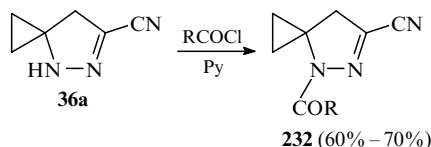
Thermolysis of the azimines **224** and **226** (*o*-dichlorobenzene, 170 °C) results in the elimination of one nitrogen molecule to give fused heterocyclic systems (compounds **228a,b**) with retention of the cyclopropane fragment; in addition, deeper partial dedinitrogenation of the azimines to give spiropentane derivatives **229a,b** is observed.³² It is assumed¹⁴¹ that spiro[cyclopropanetetrahydropyrazolo[1,2-*b*]phthalazine}diones **228** are formed due to the preliminary dissociation of azimines **224**, **226** to the starting dihydropyrazoles **32a**, **35** and phthalimidonitrene **230**. The nitrene **230** eliminates a nitrogen molecule to give benzocyclobutenedione

231, which is in equilibrium with its open diketene form. The latter reacts with dihydropyrazoles **32**, **35** to give compounds **228a,b** in 25%–28% yields. The 4,5-dihydro-3*H*-pyrazoles formed upon the destruction of azimines undergo dedinitrogenation to give the corresponding spiropentanes **229a,b**.

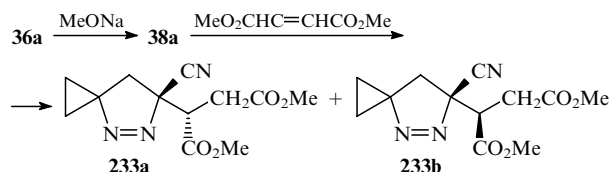


$R^1 = \text{H}$, $R^2 = \text{Ph}$ (**a**); $R^1 = \text{Me}$, $R^2 = \text{COOMe}$ (**b**).

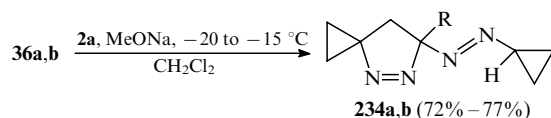
3-Cyanospiro[cyclopropane-4,5-dihydro-1*H*-pyrazole] **36a**, like other 4,5-dihydro-1*H*-pyrazoles, can be acylated with benzoyl or cyclopropanoyl chloride in the presence of pyridine to give 1-acyl-4,5-dihydro-1*H*-pyrazoles **232**.¹⁴² On the other hand, the anions **38a,b** generated from 4,5-dihydro-1*H*-pyrazoles **36a,b** add to alkenes containing electron-withdrawing substituents exclusively as C(3)-nucleophiles [compounds **37a,b** are formed similarly (see Section II)].³⁶ For example, dihydropyrazole **36a** reacts with dimethyl maleate or dimethyl fumarate in the presence of MeONa to give a mixture of diastereomeric cyanodiester **233a,b** (ratio ~ 1.5 : 1, overall yield ~ 70%).^{37,38}



$R = \text{Ph}$, cyclo- C_3H_5 .



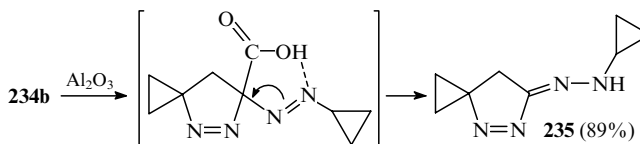
Unexpectedly, spiro[cyclopropane-1,5'-4,5-dihydro-1*H*-pyrazoles] **36a,b** readily react with diazocyclopropane (**1**) generated *in situ*. For example, decomposition of cyclopropylnitrosourea (**2a**) on treatment with MeONa or K_2CO_3 in the presence of dihydropyrazoles **36a,b** results in hitherto unknown (*E*)-cyclopropylazodihydropyrazoles **234a,b** as the main reaction products.^{36,42} A reaction scheme was suggested which is similar to that of the formation of azo compounds through azo-coupling of aromatic diazonium salts with various substrates, including 4,5-dihydro-1*H*-pyrazoles.¹⁴³ The reaction of the **38a,b** anions can probably involve diazocyclopropane precursors such as cyclopropyldiazohydroxide or the cyclopropyldiazonium cation formed upon alkaline decomposition of nitrosourea **2a**, rather than compound **1** itself.¹ This scheme is supported by the fact that aliphatic diazo compounds, *e.g.* diazomethane or methyl diazoacetate, do not enter into similar reactions with 4,5-dihydro-1*H*-pyrazoles **36a,b**.



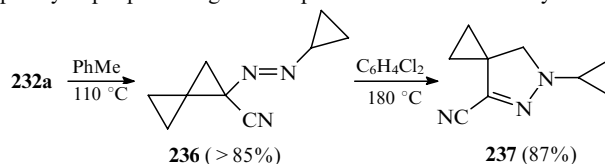
$R = \text{CN}$ (**a**), COOMe (**b**).

It should be noted that azodihydropyrazoles **234a,b** can be obtained in one step by treating acrylonitrile or methyl acrylate with a two- to three-fold excess of cyclopropylnitrosourea (**2a**).³⁶

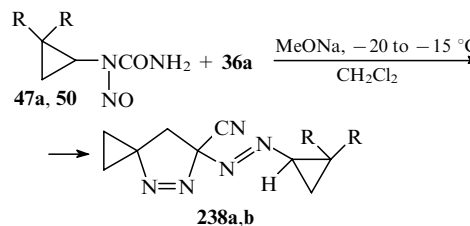
An attempt at isolation of azodihydropyrazole **234b** by TLC on Al_2O_3 resulted in its transformation to cyclopropylhydrazone **235** (probably due to hydrolysis of the ester groups followed by decarboxylation); the spiro[cyclopropane-1,5'-4,5-dihydro-3*H*-pyrazole] structure is retained under these conditions.



Thermolysis of azodihydropyrazole **234a** (110 °C, 2 h) is accompanied by elimination of the ring nitrogen atoms to give 1-cyano-1-(cyclopropylazo)spiro-pentane (**236**), which undergoes azocyclopropane–dihydropyrazole rearrangement at higher temperature (180 °C, 40 min)^{144,145} to give dihydropyrazole **237** with a spirocyclopropane fragment at position 4 of the heterocycle.³⁶

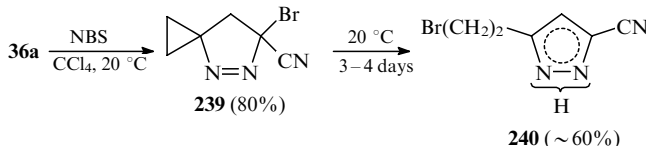


Substituted diazocyclopropanes generated by decomposition of *N*-nitrosoureas **47a** or **50** on treatment with sodium methoxide react with dihydropyrazole **36a** similarly to the unsubstituted compound **1** to give (*E*)-azodihydropyrazoles **238a** or **238b** (each as a mixture of two diastereomers in the ratio ~ 1 : 1).⁴²

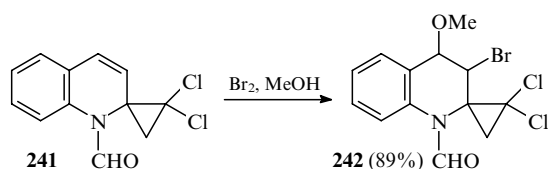


$R = \text{Me}$ (**238a**, 70%); $R-R = \text{CH}_2\text{CH}_2$ (**238b**, 65%).

Bromination of cyanodihydropyrazole **36a** with *N*-bromosuccinimide (NBS) at 20 °C in the absence of radical initiators occurs at position C(3) of the heterocycle to give 3-bromo-3-cyanospiro[cyclopropane-1,5'-4,5-dihydro-3*H*-pyrazole] (**239**) in high yield. However, the resulting bromodihydropyrazole **239** has low stability and is transformed to the isomeric (2-bromoethyl)cyanopyrazole (**240**) in 3–4 days at room temperature.¹⁴²

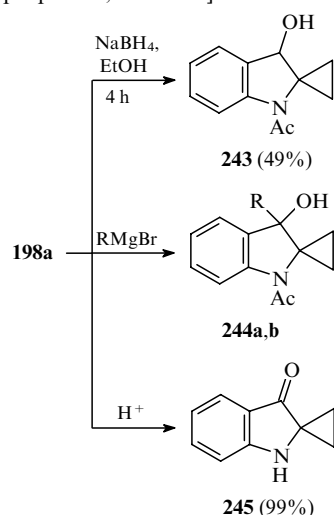


The introduction of chlorine atoms in the cyclopropane ring makes it more stable with respect to electrophilic reagents, in particular Br_2 in methanol; this enables functionalisation of the heterocyclic part of the molecule. For example, bromomethoxylation of a quinoline derivative **241** at room temperature affords a high yield of compound **242** which retains the spiro-fused cyclopropane fragment.¹⁴⁶



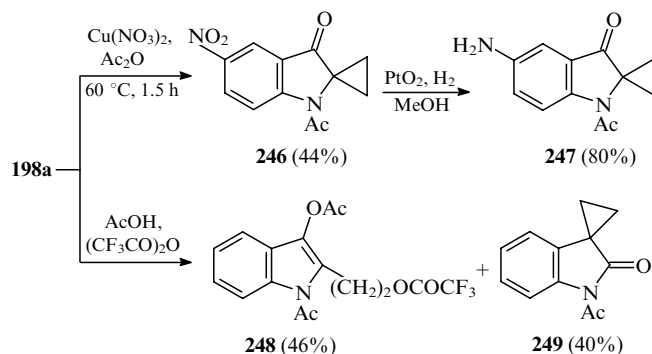
Certain transformations of spiro[cyclopropane-1,2'-indolin]-3-one derivatives, in particular of compounds **198**, also occur with retention of the cyclopropane fragment; some functional derivatives showing antiinflammatory and analgesic activities were synthesised from them.^{100, 128} For example, the reduction of compound **198a** with sodium borohydride results in the hydroxy derivative **243**; its reactions with Grignard reagents give alcohols **244a, b**.

Saponification of *N*-acetylindolinone **198a** on treatment with MeONa or KOH in methanol results in unsubstituted spiro[cyclopropane-1,2'-indolin]-3-one **245** in an almost quantitative yield. The latter was used as the starting compound for the syntheses of alkyl-, acyl-, alkoxy carbonyl- and sulfonylspiro[cyclopropane-1,2'-indolin]-3-ones.¹²⁸



R = Ph (**244a**, 67%), Bn (**244b**, 79%).

Nitration of compounds **198a** with copper nitrate gives the 5-nitro derivative **246**, catalytic hydrogenation of which affords 5-aminoindolinone **247**. The acetyl amino and mesitylamino derivatives of the latter show biological activities. It is of note that treatment of the spirane compound **198a** with trifluoroacetic anhydride in acetic acid results not only in cyclopropane ring opening to give substituted indole **248**, but also in skeletal isomerisation of compound **198a**, probably through Wagner–Meerwein rearrangement. The rearrangement product **249** is formed in 40% yield.¹⁰⁰



V. Conclusion

It is evident from this review that the methods for the synthesis of nitrogenous heterocycles containing a spirocyclopropane fragment are quite diverse though rather laborious; this restricts considerably the study of the properties of these compounds. The interest in heterocyclic compounds incorporating a spiro-fused cyclopropane fragment stems from the search for new medicines and biologically active compounds. Some heterocycles with a spirocyclopropane fragment, such as derivatives of dihydroisoxazoles, indoline-2(3)-ones, cephalosporins and penicillanates, are of interest as potential pharmaceutical compounds.

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Incommensurate suprastructures: new problems of inorganic solid-state chemistry

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Abstract. Data on a new class of inorganic incommensurate intergrowth suprastructures, *viz.*, layered misfit compounds, are surveyed and systematised. Physical properties of misfit suprastructures are discussed. Possible mechanisms of the effects of the electronic structure and incommensurability on the structural elements of suprastructures and on their recognition in molecular ensembles are considered. The general criteria for self-organisation of incommensurate suprastructures are proposed and conditions for the fragmentation of one of the sublattices (*i.e.*, conditions for the formation of nanocomposites) are given. The bibliography includes 82 references.

I. Introduction

The term 'supramolecular chemistry' was introduced by the Nobel laureate J-M Lehn in 1978. He defined this field as the chemistry beyond the molecule, which describes complex aggregates formed as a result of association of two (or more) chemical species linked by intermolecular forces.¹ In succeeding years, this new interdisciplinary science whose language, definitions and concepts are still in their developmental stage has been progressing rapidly.²

It should be noted that the range of subjects studied in supramolecular chemistry is being steadily extended, which generates a need for the discussion of some limitations on their choice, in particular, restrictions imposed by the requirements of the geometric and topological correspondence of structural elements upon self-organisation of supramolecular ensembles. As shown below, these limitations are of fundamental importance particularly in the case of inorganic suprastructures because their structures are substantially affected by the rigidity of conjugated extended structural elements. Thus it was demonstrated³ that a guest–host system, which governs differences in the principles of construction of supramolecules based on the structural organisation of the host (three-, two-, one- or zero-dimensional structures),

is better suited to the classification of inorganic subjects of supramolecular chemistry.

Incommensurability between a guest and a host is rather frequently observed in inorganic guest–host systems, which can lead to structural and morphological changes in the supramolecular ensemble as a whole. The problem of incommensurability has been stated and considered in most detail within the framework of supramolecular chemistry dealing with incommensurate intergrowth structures. Studies in this field were started more than a decade ago.⁴ Among these structures are inorganic compounds with crystal lattices consisting of two (or more) sublattices whose periods are noticeably different (at least in one direction). The term 'misfit' is finding increasing use for the description of such compounds.

Two types of compounds with incommensurate structural elements, *viz.*, linear (one-dimensional) and layered (two-dimensional) structures, are known.⁵ Systems characterised by a one-dimensional (chain) structure of the guest sublattice (substructure) belong to the linear type (these structures are also said to be columnar misfit structures). Generally, the sizes of the 'columns' correspond to the size of the host matrix in the *ab* plane perpendicular to the axis of the column, whereas the incommensurability is associated with its *c* axis. These structures are exemplified in crystals of $\text{Hg}_{3-x}\text{AsF}_6$ containing $-\text{Hg}-\text{Hg}-$ chains, which are located in cavities formed by AsF_6 octahedra,⁴ and in compounds of the $\text{A}_{1-x}\text{Cr}_2\text{X}_{4-x}$ series ($\text{A} = \text{Ba}, \text{Sr}, \text{Eu}$ or Pb ; $\text{X} = \text{S}$ or Se ; $x = 0.29$).⁶ The structure of one compound of this series, *viz.*, $\text{Eu}_{1-x}\text{Cr}_2\text{Se}_{4-x}$, is shown in Fig. 1. This compound is of interest because it contains two types of one-dimen-

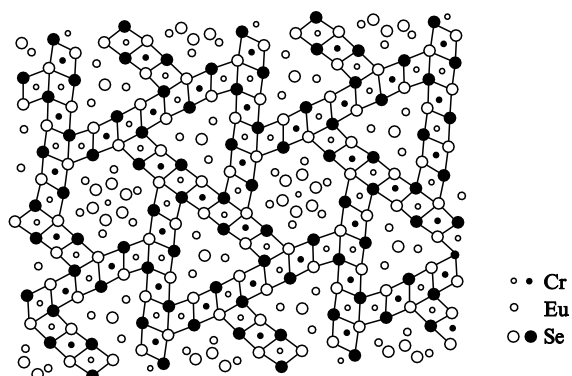


Figure 1. Structure of $\text{Eu}_{1-x}\text{Cr}_2\text{Se}_{4-x}$ (projection along the incommensurate axis).⁵

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sional guest sublattices, *viz.*, $\text{Eu}_6\text{Cr}_2\text{Se}_6$ and Eu_3Se , which thread the framework of the host $\text{Cr}_{21}\text{Se}_{36}$.

Suprastructures with incommensurate layers belong to layered misfit structures. In these structures, as in columnar misfit substances, the incommensurability is manifested only in one crystallographic direction along which the layers are aligned. These subjects are not new, since different combinations of crystallographically incommensurate layers (for example, gallium adsorbate on the surface of single-crystal silicon⁷ and some other epitaxial systems) have long been known and have been well characterised. Among layered misfit structures, synthetic complex chalcogenides of the general formula $(\text{MX})_{1+x}(\text{TX}_2)_m$ ($\text{M} = \text{Sn, Pb, Bi, Sb}$ or Ln ; $\text{T} = \text{Ti, V, Nb, Ta}$ or Cr ; $\text{X} = \text{S}$ or Se ; $x = 0.08\text{--}0.28$; $m = 1, 2, 3, \dots$) have been studied in most detail. These compounds represent analogues of the well-known minerals, *viz.*, cylindrite $[(\text{Pb,Sb})\text{S}]_{1.38}(\text{Sn,Fe})\text{S}_2$,⁸ franckeite $\text{Pb}_5\text{FeSn}_3\text{Sb}_2\text{S}_{14}$ (see Ref. 9) and some other minerals.¹⁰

The rather high thermodynamic stability of inorganic incommensurate compounds calls for revision of the existing concepts of the topological 'laws' of construction of supramolecular structures. When constructing incommensurate structures, researchers face two problems. The first problem is associated with the limiting values of the incommensurability up to which the structural elements (substructures) retain their capacity for self-organisation. The second problem is related to the consequences of this self-organisation. In the course of self-organisation of the suprastructure, forces responsible for the retention of the rigidity of its constituent substructures compete with forces linking these substructures to form a single suprastructure. This competition leads to various structural and morphological changes in the ensembles formed.

Since the discovery of incommensurate intergrowth structures, no structures possessing the incommensurability in more than one crystallographic directions have been found, *i.e.*, the topological principles of the construction of these compounds are rejected only partially. Nevertheless, even 'one-dimensional' incommensurability gives rise to very interesting properties of inorganic crystal structures.

On the whole, problems associated with the structures, phase stabilities and properties of incommensurate intergrowth suprastructures have not been adequately investigated, though, in our opinion, these problems are of importance for both inorganic supramolecular and solid-state chemistry.

In particular, one of the fruitful lines of investigation of incommensurate structures may be associated with an apparent analogy of the mechanisms of formation of intercalates A_xTX_2 (A is a donor species and TX_2 is a layered dichalcogenide matrix) to those of layered misfit compounds (with the same matrices).

It is also worthy of note that studies dealing with layered misfit compounds have been aimed mainly at searching for new combinations of incommensurate substructures, developing procedures for their structural identification and studying their physical properties. We believe that studies of layered misfit structures are of interest not only because of unusual properties of these compounds, but primarily because of considerable prospects of their application due to evident possibility of the preparation of materials possessing unique electrophysical and magnetic characteristics (if only due to the nontrivial behaviour of conduction electrons in incommensurate crystal fields).

II. Synthesis and structures of misfit compounds

Several procedures for the synthesis of incommensurate suprastructures are known. The majority of layered misfit structures $(\text{MX})_{1+x}(\text{TX}_2)_m$ have been prepared by solid-phase high-temperature synthesis starting from the elements or the corresponding binary compounds (MX and TX_2). Generally, suprastructures with $\text{M} = \text{Sn, Pb, Bi}$ or Sb are formed at about $800\text{--}900^\circ\text{C}$,^{11–16} whereas suprastructures with $\text{M} = \text{Ln}$ are formed at 1050--

1350°C .^{17–20} In all cases, the syntheses are completed in several days.

In a number of studies, layered misfit structures were prepared by slow heating of the starting mixtures to temperatures at which the synthesis started. Then the mixtures were kept at this temperature for several days and the resulting specimens were slowly cooled. Procedures for the synthesis of layered misfit compounds involving quenching of specimens from high temperatures (see, for example, Refs 12 and 16) were also reported. Unfortunately, the dependence of the properties of the resulting specimens on the mode of cooling was not examined.

Most of the known misfit compounds were prepared using stoichiometric amounts of chalcogenides MX and TX_2 ($1:m$) based on the formula $(\text{MX})(\text{TX}_2)_m$ (*i.e.*, at $x = 0$), although the compositions of the resulting substances are described by the formula $(\text{MX})_{1+x}(\text{TX}_2)_m$, where x is distinct from zero. Generally, syntheses of misfit compounds from the elements were carried out using a small excess of the corresponding chalcogen to accelerate the reaction (see, for example, Ref. 15).

A procedure for the preparation of layered misfit suprastructures (especially, based on REE) from the corresponding ternary oxides by their heating in a graphite boat under a stream of a mixture of hydrogen sulfide and an inert gas at $1300\text{--}1350^\circ\text{C}$ was also described.⁵ In particular, this procedure was used for the preparation of $(\text{LaS})_{1.19}\text{CrS}_2$.

Single-crystalline specimens can be synthesised by the transport reaction method. Traditionally, iodine^{19,20} or chlorine¹⁴ serves as the transporting agent. (It was mentioned that crystals were formed in the cooling zone of a furnace.) Crystals of 'PbNbS₃' and 'LaNbS₃' were grown with the use of an admixture of $(\text{NH}_4)_2\text{PbCl}_6$, which decomposed at high temperature to form PbCl_2 , NH_4Cl and Cl_2 .¹⁷ Apparently, the chlorine liberated acted as the transporting agent.

As mentioned above, layered misfit suprastructures of the $(\text{MX})_{1+x}(\text{TX}_2)_m$ type consist of layers of two substructures, *viz.*, MX (guest) and TX_2 (host). The guest layer (Q layer) has a pseudocubic NaCl-type lattice and the host layer (H layer) represents a 'sandwich' of hexagonal networks built up from X atoms. Atoms of the transition metal T are either in trigonal-prismatic (Nb or Ta) or octahedral (Ti, V or Cr) environment formed by X atoms (Figs 2 and 3).^{21–24} Thus the trigonal-prismatic and octahedral environments about the T atoms are observed in the structures $(\text{SnS})_{1.17}\text{NbS}_2$ (see Ref. 24) and $(\text{PbS})_{1.18}\text{TiS}_2$,²¹ respectively.

Layered misfit compounds differ in the number of the host layers per guest layer (for example, $1\text{Q}/1\text{H}$, $1\text{Q}/2\text{H}$ or $1\text{Q}/3\text{H}$).⁵ Therefore, these compounds are described by the general formula $(\text{MX})_{1+x}(\text{TX}_2)_m$, where the index m is the number of TX_2 layers per unit cell of the suprastructure along the c axis. Mono- ($m = 1$) and bilayer ($m = 2$) structures (Fig. 4) prevail. The arrangement of the structural elements along the b axis can also be different due to the presence of two extreme stacking sequences for the substructures. In the case of a body-centred (CC) arrangement of MX and TX_2 substructures, their c axes coincide, whereas in the case of a face-centred (FF) arrangement, these axes are shifted

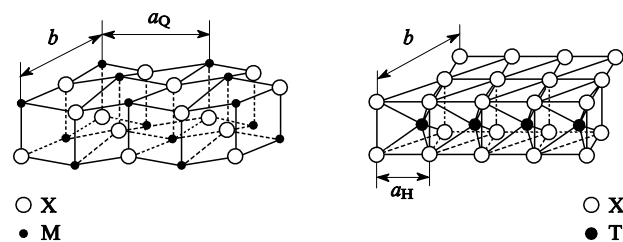


Figure 2. Substructures MX (Q layer) and TX_2 (H layer) with incommensurate lattice parameters (a_Q and a_H).

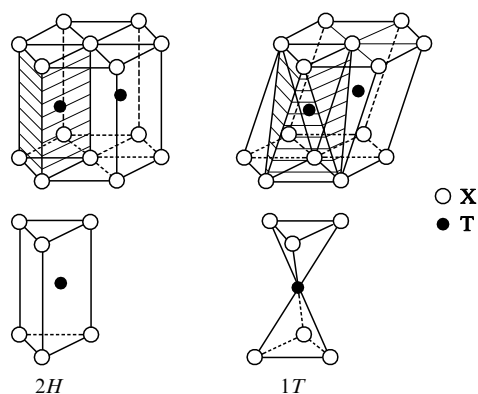


Figure 3. Coordination of the T atoms in the trigonal-prismatic ($2H$) and octahedral ($1T$) polytypes of the TX_2 substructure.

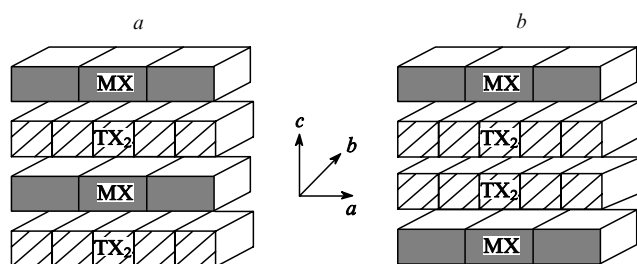


Figure 4. Schematic representation of monolayer (a) and bilayer (b) misfit structures.

relative to each other by $a/2$. Intermediate modes (CF and FC) of arrangement of MX and TX_2 units were also found (Fig. 5).⁵

The limiting stoichiometry of the suprastructure $(MX)_{1+x}(TX_2)_m$ as a whole is determined by the ratio between the parameters a of the host and the guest (a_H/a_Q), which can change from 0.64 [for $(YS)_{1.28}CrS_2$]²² to 0.54 [for $(BiS)_{1.08}TaS_2$].²³ Here, $x = (4/2)(a_H/a_Q) - 1$ ($4/2$ is the ratio between the numbers of the MX and TX_2 formula units in the unit cell of the suprastructure). The parameters a_H and a_Q of the unit cells of selected layered misfit compounds are given in Table 1.

The application of the X-ray powder method and X-ray structural analysis to studies of misfit structures presents problems because the symmetry of these compounds should be described by four-dimensional space groups.^{4,17} It was also demonstrated that the precise identification of misfit structures is complicated by the following interrelating facts: by the presence of

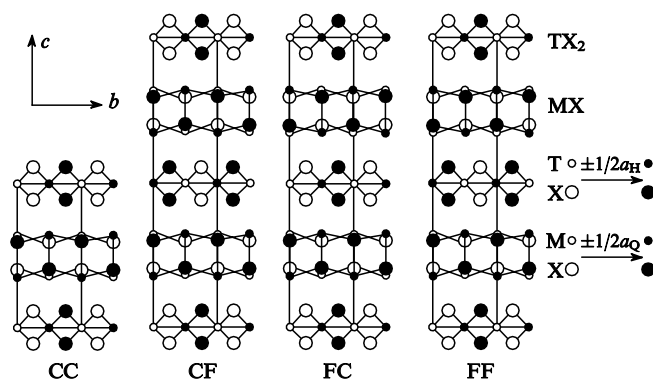


Figure 5. Different structural types of layered misfit compounds based on NbS_2 and TaS_2 (projections along the $[100]$ direction).⁵

Table 1. Limiting stoichiometric ratios for the unit cells of some layered misfit compounds.

Compound	$a_Q/\text{\AA}$	$a_H/\text{\AA}$	$x = 2a_H/a_Q - 1$	$b_Q = b_H/\text{\AA}$	Ref.
$(SnS)_{1.17}NbS_2$	5.673	3.321	0.1708	5.751	24
$(LaS)_{1.14}NbS_2$	5.828	3.310	0.1359	5.797	17
$(PbS)_{1.18}TiS_2$	5.800	3.410	0.1755	5.881	21

several polytypes in the suprastructure, which hinders the formation of single crystals, and by the difference in morphology of crystalline particles of these suprastructures. Thus it was found that the synthesis and prolonged annealing (required for the attainment of thermodynamic equilibrium) of the misfit compounds $(BiS)_{1+x}(NbS_2)_m$ and $(PbS)_{1+x}(NbS_2)_m$ gave rise both to the usual layered crystals and species with the same composition, which resemble an insulation tape bundle.^{11,15} Beginning with a particular diameter of the species, the layers are twisted and the maximum radius of the bundle does not exceed 0.1 mm.

III. Physical properties of misfit suprastructures

The complexity of incommensurate suprastructures (in particular, layered misfit structures) and the characteristic features of interactions between their constituent substructures result in the diversity of the physical properties observed. Misfit structures are studied by different physical and physicochemical methods. The electrophysical and magnetic properties of misfit compounds were examined in a large number of studies. The superconductivity of compounds based on some layered dichalcogenides with the $2H$ structure was also investigated. Valuable information on the physical properties of incommensurate suprastructures was also obtained in studies of X-ray photoelectron spectra, optical reflectance and Raman spectra as well as in studies with the use of some other methods.

1. Electrophysical properties

Misfit compounds containing NbX_2 or TaX_2 as the host substructure possess metallic conductivity.^{11,13,19,23–26} In these structures, the resistivity (ρ_{ab}) in the ab plane is $\sim 10^{-6} \Omega$.^{19,23–27} The ratio between the resistivities along the commensurate (b) and incommensurate (a) axes (ρ_a/ρ_b) is close to unity [for example, in the compound $(CeS)_{1.16}NbS_2$].²⁷ This is also evident from the number of charge carriers along the a and b axes calculated for the suprastructure $(PbS)_{1.13}TaS_2$. These values were determined from optical reflectivity measurements.²⁸ The resistivity along the c axis is substantially larger than that in the ab plane. The ρ_c/ρ_{ab} ratio is equal to 50 for compounds based on chalcogenides of rare-earth elements²⁷ and it is even larger for suprastructures with $M = Sn, Pb$ or Bi . Thus the ρ_c/ρ_{ab} ratio for $(SnS)_{1.18}NbS_2$ is 250 and 800 at 300 and 4 K, respectively.³ ($\rho_c/\rho_{ab} \approx 10^5$ determined at 300 K for this compound previously²⁴ is, apparently, overestimated).

Like some intercalates based on tantalum and niobium dichalcogenides, misfit suprastructures formed from TaS_2 or NbS_2 and PbS, SnS or BiS are characterised by a positive Hall coefficient and a negative Seebeck coefficient.^{23–26} The number of holes calculated from the Hall coefficients at 4 K^{25,26} suggest the occurrence of electron transfer from the MX layers to the TX_2 layers in incommensurate suprastructures, as in intercalates, the d_{z^2} band of the TX_2 layer being more than half-filled. Taking into account the negative Seebeck coefficients, it should be noted that these data are only tentative.

Suprastructures consisting of TaX_2 or NbX_2 layers and layers of REE chalcogenides are characterised by a substantially lower concentration of charge carriers compared to suprastructures containing Sn, Pb or Bi chalcogenides. These compounds possess positive Hall and Seebeck coefficients,^{29–31} which is indicative of p-type conductivity in these compounds. The calculated degrees of electron density transfer in suprastructures with $M = REE$ are

substantially higher than those observed in compounds with $M = \text{Sn}$ or Pb .³¹ The X-ray photoelectron spectra of these compounds^{32–35} also revealed an essential electron transfer from MX to TX_2 layers. In this case, the M atoms exist virtually in the trivalent state.

Metallic conductivity is also typical of suprastructures $(\text{MS})_{1+x}(\text{TiS}_2)$ with $M = \text{Sn}$ or Pb .^{11,36,37} The temperature dependences of ρ_{ab} observed for $(\text{MS})_{1+x}(\text{TiS}_2)$ ³⁶ is analogous to those found for the intercalates Li_xTiS_2 (see Ref. 38) and Ag_xTiS_2 .³⁹ The Hall coefficient of the former is negative and corresponds to the partial filling of the conduction band of the TiS_2 substructures by electrons from the MX substructure. However, the character of the temperature dependence of ρ_{ab} indicates that holes in the valence band of MX are not involved in the conductivity. It was thus suggested⁵ that holes are localised in the valence band of the MX substructure. This localisation occurs either due to a change in the lattice potential along the $[100]$ direction giving rise to centres of hole localisation or due to the presence of defects and vacancies in the MX sublattice.

The compounds $(\text{CeS})_{1.19}(\text{TiS}_2)_m$ ($m = 1$ or 2)³⁷ also possess metallic conductivity and exhibit antiferromagnetic ordering at 2.8 K, which is not accompanied by anomalous behaviour of the conductivity around this point. This indicates that the MX layers do not contribute to the conductivity of the above-mentioned compounds. The residual resistivities observed for the compounds $(\text{CeS})_{1.19}(\text{TiS}_2)_m$ (~ 450 and $350 \mu\Omega \text{ cm}$ for $m = 1$ and 2 , respectively) are larger than that for Li_xTiS_2 (see Ref. 38) whose structure is not incommensurate. The authors believed that this fact is indicative of a substantial effect of the incommensurability of misfit structures on the crystal lattice, which is manifested in its local modulations playing a significant role in scattering of charge carriers.³⁷

The majority of compounds with the VX_2 sublattice, for example, $(\text{PbS})_{1.12}\text{VS}_2$ (see Ref. 12) and $(\text{LnS})_{1+x}\text{VS}_2$ (see Refs 37 and 40) ($\text{Ln} = \text{La}, \text{Ce}, \text{Nd}$ or Sm), exhibit semiconducting properties. It was found that the conductivity of the compounds $(\text{LnS})_{1+x}\text{VS}_2$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$ or Nd) changed from semiconducting to metallic at 150–200 K.⁴¹

The $V-V$ distances in the misfit compound $(\text{PbS})_{1.12}\text{VS}_2$ possessing semiconducting properties⁴² are close to those in the intercalates Na_xVS_2 ,⁴³ which exhibit metallic conductivity. Therefore, the semiconducting properties of $(\text{PbS})_{1.12}\text{VS}_2$ demonstrate that holes in the valence band of PbS are not involved in the conductivity. These holes are either localised or absent due to lattice defects. X-ray structural analysis of the compound $(\text{LaSe})_{1.21}\text{VSe}_2$ within four-dimensional symmetry space groups⁴⁴ established that the LaSe sublattice contains $\sim 5\%$ of lanthanum vacancies and the VSe_2 sublattice is characterised by a large modulation of the $V-V$ distances giving rise to centres of localisation of charge carriers. Therefore, holes available in the valence band of LaSe layers do not contribute to the conductivity of the compound $(\text{LaSe})_{1.21}\text{VSe}_2$. Based on the conductivity data, the temperature dependence of the thermoelectric power and the optical reflectivities for the compound $(\text{LaS})_{1.16}\text{VS}_2$, it was concluded that charge carriers are localised in LaS layers.³⁷

Misfit suprastructures with the CrS_2 host substructure were prepared only for REE. The measurements of the conductivity of $(\text{GdS})_{1.27}\text{CrS}_2$ (see Ref. 45) demonstrated that this compound exhibits semiconducting properties; the activation energy is 0.34 eV. The suprastructure $(\text{LaS})_{1+x}\text{CrS}_2$ also possesses semiconducting properties.^{45,46} The X-ray photoelectron spectra and magnetic measurements performed for the compounds $(\text{LnS})_{1+x}\text{CrS}_2$ demonstrated that chromium atoms occupying the CrS_2 sublattice points exist in the trivalent state,^{47,48} which is indicative of a substantial electron transfer from LnX layers to CrS_2 layers. In this case, a portion of electrons (x) does remain in the LnX sublattice, which seemingly should give rise to metallic conductivity in these misfit compounds (at least, for elements of the first part of the REE series whose electrons are delocalised over $5d$ and $4f$ orbitals). However, the precise chemical analysis of

the compound $(\text{LaS})_{1+x}\text{CrS}_2$ (see Ref. 45) demonstrated that the lanthanum content in this compound is less than that expected. Based on the results of the analysis, the formula $(\text{La}_{0.94}[\text{La}_{0.06}\text{S}])_{1.2}\text{CrS}_2$ was assigned to the compound $(\text{LaS})_{1+x}\text{CrS}_2$ because the charges of La^{3+} , Cr^{3+} and S^{2-} can be balanced out only if lanthanum vacancies are present in the LaS layers. An analogous situation was observed for the compound $(\text{GdS})_{1.27}\text{CrS}_2$ to which the composition $(\text{Gd}_{0.91}[\text{La}_{0.09}\text{S}])_{1.27}\text{CrS}_2$ was assigned on the basis of the data from precise chemical analysis and X-ray structural analysis. In this case, charge balance between the ions is observed. Therefore, the semiconducting character of the compounds under consideration is attributable to partial localisation of electrons in the MX layers.

2. Magnetic properties

The magnetic properties of layered misfit compounds based on TaX_2 or NbX_2 with the LnX guest substructure are determined primarily by the nature of the Ln atom. The strong effect of the crystal field was observed for mono- and bilayer misfit structures with $M = \text{Ce}$ or Nd .^{19,27,34,49} Studies of the magnetic properties of the compounds $(\text{LnS})_{1+x}(\text{TS}_2)_m$ ($T = \text{Ta}$ or Nb) demonstrated that these properties are substantially different in the directions perpendicular and parallel to the magnetic field (the direction of the field coincides with the c axis of the crystal). Thus the magnetic susceptibilities for the phases ' NdNb_2S_5 ' and ' SmNb_2S_5 ' along the field and in the transverse direction differ by factors of 1.5 and 2.5–2.6, respectively.¹⁹ The small magnetic moments of the compounds $(\text{LaX})_{1+x}(\text{TX}_2)_2$ (see Refs 19, 49 and 50) indicate that lanthanum atoms exist in the trivalent state, which is indicative of a substantial electron transfer from LaX layers to TX_2 layers. In suprastructures with $M = \text{Ce}$ ⁵¹ or Sm ,³⁴ the electron density transfer from MX layers to TX_2 layers is somewhat smaller than that observed in suprastructures with $M = \text{La}$. According to the results of measurements of magnetic moments, weak ferromagnetic interactions occur within the LnX layer and even weaker antiferromagnetic interactions occur between the LnX layers. At low temperature, antiferromagnetic ordering is observed in suprastructures (in this case, the temperature dependence of the magnetic moment does not obey the Curie–Weiss law).^{19,38,45} For the suprastructure ' GdNb_2S_5 ', the ordering occurs at 5 K.¹⁹ For the suprastructure $(\text{GdS})_{1.21}\text{NbS}_2$, the ordering occurs at 12.8 and 4.6 K.³⁸ Somewhat different results were obtained for compounds with $M = \text{Tb}$, Dy or Er . At low temperature, these compounds behave as paramagnetics and do not exhibit the anisotropy of magnetic properties.^{5,19} This was attributed to the absence of the effect of the crystal field in the case of REE atoms located in the right part of the Periodic system due to a larger contraction of their $4f$ orbitals.

The magnetic properties of the suprastructures $(\text{LnS})_{1+x}\text{VS}_2$ also substantially depend on the nature of the Ln atom^{40,52} and are in many respects similar to the properties of the corresponding structures based on NbX_2 . However, the properties of the former compounds are distinguished by stronger antiferromagnetic interactions between LnS layers. The deviation of the temperature dependence of the magnetic moment from the Curie–Weiss law at low temperatures is attributed to the effect of the crystal field. The magnetic properties of the compounds $(\text{LnS})_{1+x}\text{VS}_2$ indicate that the Ln atoms in these compounds exist in the trivalent state.

The magnetic behaviour of misfit structures containing CrS_2 layers is more complex because of the contribution of Cr^{3+} ions.^{45,47,48} Thus the compound $(\text{LaS})_{1.20}\text{CrS}_2$ behaves as a paramagnetic up to 110–300 K. At low temperatures, two magnetic transitions (at 120 and 70 K) are observed for this compound.⁴⁸ Such behaviour of $(\text{LaS})_{1.20}\text{CrS}_2$ is conditioned by the spins of the Cr^{3+} ions. The results of magnetic measurements for structures containing CrS_2 layers were interpreted taking into account the type of ordering of the magnetic structure at low temperature and possible antiferromagnetic interactions between the Cr ions in the CrS_2 layer (depending on the $\text{Cr}-\text{Cr}$ distance) (see, for example, the review⁵).

3. Superconductivity

Of the known misfit suprastructures, only the compounds $(MX)_1 + x(TX_2)_m$ ($M = \text{Sn, Pb, Bi or Ln}$; $X = \text{S or Se}$, $m = 1$ or 2) based on layered tantalum or niobium dichalcogenides, which have $2H$ structures and possess their own superconductivity, exhibit superconducting properties. The superconducting transition critical temperatures (T_c) for all these misfit compounds are lower than those for the corresponding dichalcogenides TX_2 , which is, apparently, attributable to the insulating properties of MX layers.^{53–58} For example, the T_c values for the compounds $(\text{PbS})_{1.14}(\text{NbSe}_2)_2$ and $(\text{PbS})_{1.14}\text{NbSe}_2$ are 3.4⁵⁴ and 2.475 K,⁵³ respectively, whereas T_c for $2H\text{-NbSe}_2$ is 6.3 K.⁵ Misfit compounds based on TX_2 , like dichalcogenides as such, exhibit anisotropy of the critical field, which depends on the nature of the metal M . Thus the anisotropy is ~ 1.29 and 35 for $(\text{BiSe})_{1.10}\text{NbSe}_2$ and $(\text{LaSe})_{1.14}\text{NbSe}_2$, respectively. For mono- and bilayer suprastructures, the critical fields also have differing anisotropy. For the monolayer compounds $(\text{SnS})_{1.17}\text{NbS}_2$ and $(\text{PbS})_{1.14}\text{NbS}_2$, the anisotropy is $\sim 8–10$,^{53, 56} whereas the anisotropy for the bilayer compound $(\text{PbSe})_{1.12}(\text{NbSe}_2)_2$ is $\sim 4–5$.⁵⁴ Based on the fact that the compound $(\text{PbSe})_{1.12}(\text{NbSe}_2)_2$ exhibits anisotropy intermediate between those of $(\text{PbS})_{1.14}\text{NbS}_2$ and NbSe_2 as such, it was suggested that the compound $(\text{PbSe})_{1.12}(\text{NbSe}_2)_2$ is a second-stage intercalate.⁵⁷

* * *

To sum up the discussion of the physical properties of layered misfit structures, it should be stated that these properties can be described to a first approximation by an additive scheme, *viz.*, as a result of superposition of the properties of the TX_2 and MX substructures. Thus studies of a number of misfit structures by X-ray photoelectron and Raman spectroscopy^{21, 59–62} demonstrated that these spectra can be described as a superposition of the spectra of the MX and TX_2 substructures.

In some respects, this is also true for the results of studies of the electrophysical properties of these compounds. When describing suprastructures $(MX)_1 + x(TX_2)_m$ within the framework of the rigid band model, one can use the fact that the TX_2 and MX layers in these structures are similar to the corresponding layers in crystals of TX_2 and MX , with the difference that the Fermi level for the TX_2 layer of the misfit structure is located higher than that in the crystal of TX_2 and taking into account that the changes in the MX layer compared to the analogous layer in the crystal are caused by the electron transfer to the TX_2 layer. (The charge transfer from the MX layers to the TX_2 layers was quantitatively evaluated based on the Hall and Seebeck coefficients.)

Needless to say the real situation goes beyond the scope of the simple additive scheme. For example, as mentioned above, the mutual effect of two substructures, which is manifested, in particular, in distortions and discontinuities of the crystal lattices of the TX_2 and MX layers, cannot be ignored. On the whole, the data on the physical properties of layered misfit structures confirm the correctness of their comparison with intercalates of the A_nTX_2 type.

IV. Interactions of substructures and phase stabilities of layered misfit compounds

In this Section, we consider the nature of the interaction between substructures and the possibility of deformation of their lattices. In our opinion, it is worthwhile to perform a comparative analysis of conditions of the occurrence of layered misfit structures $(MX)_1 + x(TX_2)_m$ and intercalates A_nTX_2 (A is any metal) because this analysis can be based on the use of a unified approach determining the limits of the phase stability of the layered TX_2 host matrix. Although intercalates, unlike misfit structures, do not imply incommensurability between the host and guest lattices (in the theory of intercalates,⁶³ it is assumed that cavities in the host lattice topotactically correspond to the structure of the guest),

both layered misfit structures and intercalates are characterised by $Q-H$ interactions of the same type determined by charge transfer from MX to TX_2 and from A to TX_2 , respectively.^{64, 65} The concept describing the conditions of phase stability of layered intercalates is based on the rigid band model.⁶⁶

Depending on the coordination of the T atom, the TX_2 matrix can exist in two structural modifications related to the electronic stabilisation of the conduction bands, *viz.*, $1T$ (octahedral coordination) and $2H$ (trigonal-prismatic coordination). The schemes of the conduction bands for layered dichalcogenides of Groups IV–VI transition metals are shown in Fig. 6.

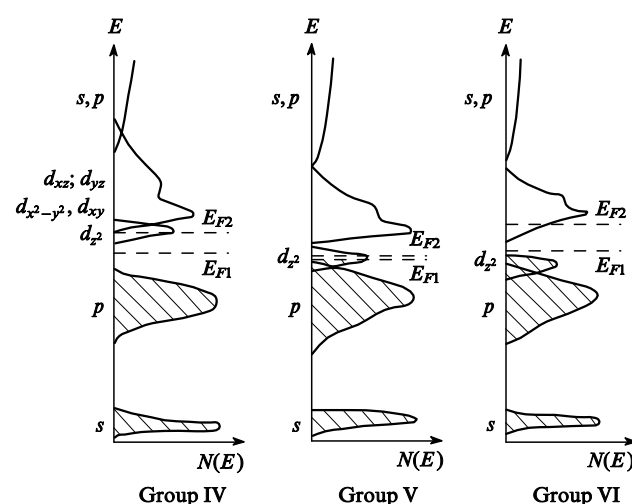


Figure 6. Band structures of transition metal dichalcogenides TX_2 ($2H$ polytype).⁶⁶

It was found⁶⁶ that the valence band of the TX_2 layer consists of two subbands to which the s and p atomic orbitals (AO) of chalcogen X make the major contributions, whereas the conduction band consists primarily of nonbonding d -AO of the transition metal T . The splitting of the conduction band by the crystal field of the X atoms determines its occupation by electrons and the energetics. In the $2H$ structures of TX_2 , the band formed by the d_{z^2} -AO of the T metal has the lowest energy.

For the d^1 ions of Group V metals (for example, for Nb and Ta), this band is half-filled; the occupied and unoccupied levels of this band are not separated due to which these compounds exhibit metallic conductivity. Within the limits determined by the filling of the d_{z^2} -AO of the T atom, intercalation of the structures $2H\text{-NbX}_2$ and $2H\text{-TaX}_2$ does not lead to electron destabilisation of the system and occurs rather readily. We have demonstrated^{67, 68} that destabilisation of the conduction band in the intercalates Ga_aNbSe_2 and Ga_aTaSe_2 occurs at $a \approx 0.12$ and is accompanied by the transformation of a two-dimensional structure into a three-dimensional (spinel) structure, which is associated with a change in the valence states of gallium and niobium (tantalum) atoms caused by charge transfer from gallium to niobium (tantalum).

Layered misfit structures $(MX)_1 + x(TX_2)_m$ based on dichalcogenides of Group V transition metals have been rather well studied. It was demonstrated that the degree of charge transfer from M to T depends on the properties of the MX guest layer.^{17, 19, 25, 26, 29–35, 49–51, 62, 64} In suprastructures containing lanthanide ($M = \text{Ln}$) sulfides (selenides) as the guest, substantial charge transfer was observed. Thus based on the temperature dependence of the conductivity and the data from X-ray photoelectron spectroscopy, it was established that the filling of the d_{z^2} band in $2H\text{-TaX}_2$ for monolayer structures is 1.8–1.97 electrons per T metal atom. A different situation occurs in misfit compounds with $M = \text{Sn or Pb}$. In the latter, the charge transfer is

significantly smaller. According to the published data,^{24, 25, 64} the charge transfer in these suprastructures is 0.3–0.5 electrons per T atom.

Apparently, suprastructures with $T = V$ are a special case.^{12, 37, 40, 44, 52, 61} In the phases $(\text{PbS})_{1.12}\text{VS}_2$,¹² $(\text{LnS})_{1+x}\text{VS}_2$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Nd}$ or Sm)^{37, 40} and $(\text{LaSe})_{1.12}\text{VSe}_2$,⁴⁴ vanadium atoms are in an octahedral environment. In these structures, as in compounds with $T = \text{Nb}$ or Ta , electron density is transferred from MX layers to VX_2 layers, this transfer being particularly significant for compounds with $M = \text{Ln}$.^{40, 52} As mentioned above, the $V-V$ distances in these misfit structures are close to those in intercalates Na_xVS_2 (see Ref. 43) possessing metallic conductivity. A consideration of the electronic structures of misfit suprastructures based on VX_2 within the framework of the rigid band model assumes that these structures possess metallic conductivity. However, most of the suprastructures synthesised based on vanadium chalcogenides are actually semiconductors. This behaviour may be attributed either to the formation of an energy gap in the Fermi level due to splitting of the t_{2g} orbitals³⁷ or to localisation of charge carriers in the MX layer at defects of different types^{37, 44, 61} caused primarily by the incommensurability of substructure lattices.

Layered matrices based on chalcogenides of Group VI metals, such as Mo and W, belong to the $2H$ polytype and are high energy-gap semiconductors. The d_{z^2} band in chalcogenides of Group VI metals with the $2H$ structure, unlike that in chalcogenides of Group V metals, is completely filled. The energy gap between this band and the nearest unoccupied levels is ~ 1.5 eV.⁶⁶ Hence, intercalation of these compounds with A donors is very hindered. Therefore, it is reasonable that layered misfit structures based on $2H$ layers of MoX_2 or WX_2 are as yet unknown. At the same time, misfit compounds based on chromium sulfide, *viz.*, $(\text{LnS})_{1+x}(\text{CrS}_2)_m$, with the $1T$ structure of the host matrix have been characterised in sufficient detail. These compounds are semiconductors with an energy gap of ~ 0.5 eV. In these compounds, as in the compounds $(\text{LnS})_{1+x}(\text{VS}_2)_m$, the M and T atoms exist in the trivalent states due to a substantial charge transfer from Ln to Cr and the presence of vacancies in Ln positions.^{37, 45, 46}

Layered misfit suprastructures with $M = \text{Bi}$ or Sb are a special case. Although these compounds are very similar in structure and properties to compounds with $M = \text{Pb}$ or Sn , the charge transfer in the former compounds determined from electrophysical data^{23, 26} is substantially smaller than that in misfit structures with $M = \text{Pb}$ or Sn , unless a strong acceptor, such as CrS_2 , serves as the host matrix.⁶⁴ The X-ray photoelectron spectra⁶⁹ of the compounds $(\text{SbS})_{1+x}\text{CrS}_2$ and the Bi–S bond lengths in $(\text{BiS})_{1.23}\text{CrS}_2$ (see Ref. 70) demonstrate that the Sb and Bi atoms in these compounds exist in the trivalent state. A number of characteristic structural features of the compounds $(\text{BiS})_{1.08}\text{TaS}_2$ and $(\text{BiS})_{1.09}\text{TaSe}_2$ containing short Bi–Bi bonds were mentioned.¹⁵

Of Group IV transition metals, only titanium atoms form layered dichalcogenide structures with a crystal lattice of the $1T\text{-CdI}$ type (with octahedral coordination about the T atom, see Fig. 3). Generally, their intercalation with donors (metals) is accompanied by a $1T \rightarrow 2H$ phase transition.⁶³ The atomic t_{2g} orbitals of titanium ions with the d^0 electronic configuration are unoccupied. However, intercalation of the TiX_2 matrix with A donor atoms leads to the electron transfer from A atoms to Ti ions and to the occupation of the t_{2g} orbitals. In this case, their degeneracy is eliminated because the trigonal-prismatic ($2H$) coordination about Ti atoms with the lower-energy d_{z^2} band becomes energetically more favourable. A rather surprising thing is that the Ti atoms retain an octahedral coordination in spite of the difference in the character of the MX layers and the conditions of charge transfer.

Titanium dichalcogenides form layered misfit compounds with Pb, Sn,^{11, 21, 36, 61, 71, 72} Ce³⁷ or Ag.⁷³ Electrophysical measurements^{36, 37} and analysis of photoelectron spectra^{21, 61, 74, 75} and

Raman spectra⁶¹ indicate charge transfer from MX layers to TiX_2 layers. The nature and bond strengths between the layers in such misfit structures were interpreted differently. Thus, in some studies^{3, 64, 69} it was assumed that the MX and TiX_2 layers are covalently bound (*viz.*, that there are covalent bonds between the M atoms of the MX layers and the X atoms of the TiX_2 layers). In other studies, it was reported that there are Coulombic interactions between the positively charged metal atoms M from the MX layers and the negatively charged chalcogen atoms from the TX_2 layers, as, for example, in the compounds $(\text{PbS})_{1.18}(\text{TiS}_2)_m$ ($m = 1$ or 2). Electron probe microanalysis of this compound⁷¹ revealed a deficiency of lead ions in the PbS layers, which was interpreted as the replacement of 8%–10% of Pb^{2+} ions by Ti^{3+} ions, which may lead to stabilisation of the misfit suprastructure. The stability of the compounds $(\text{CeS})_{1.19}(\text{TiS}_2)_m$ ($m = 1$ or 2) was estimated within the framework of the rigid band model based on the results of measurements of the electrical resistivity, thermoelectric power and optical reflectivity.³⁷

However, the results of the majority of studies, in our opinion, indicate that the interaction between the MX and TX_2 substructures occurs through charge transfer from the MX layers to the TX_2 layers. For example, calculations of the band structure of $(\text{LaS})(\text{SrS})_{0.2}\text{CrS}_2$ demonstrated⁴⁶ that there is no more or less significant charge density between the lanthanum atoms from the LaS layer and the sulfur atoms from the CrS_2 layer. On the contrary, the lone electron pairs of the sulfur atoms of the CrS_2 layer are directed toward the free space rather than toward the lanthanum atoms of the adjacent layer. In this case, the factors determining the polytype of the TX_2 layer in the resulting suprastructures remain unclear. In our opinion, the energy characteristics of the structures under consideration play here a decisive role. These characteristics can be described based on the concept of electronic stabilisation of the suprastructure. This concept was confirmed by the results of the study⁴⁵ in which the formation of defects in MX substructures due to the transfer of an excess charge from the MX layer to the TX_2 layer was experimentally observed and theoretically justified.

One would expect that intercalation of layered misfit structures with donor species will be accompanied by phase transitions associated with changes in substructures. Analogous processes were observed, for example, on the formation of intercalates of the $A_n\text{TX}_2$ type.^{67, 68} The formation of defects (discontinuities) in the MX substructure may be yet another consequence of intercalation.

As mentioned above, intercalates based on layered misfit compounds are formed due to charge transfer and filling of unoccupied levels of the suprastructure. Unfortunately, examples of the existence of such intercalates, their structural features and properties are limited in number. However, to a first approximation it can be stated that the rule of electronic stabilisation is fulfilled for these compounds, as in the case of intercalation of typical layered matrices. At the same time, it is important to keep in mind the differences associated with the charge transfer in the above-mentioned intercalates and in the corresponding misfit structures. Studies of intercalation of the suprastructures ' PbVS_3 ', ' PbTiS_3 ', ' PbTi_2S_5 ' and ' SnTiS_3 ' with lithium (from solutions of n-butyllithium in hexane at room temperature)¹⁴ demonstrated that intercalation of monolayer misfit structures occurs with greater difficulty than that of the corresponding bilayer structures. Analogous results were obtained in the study⁷⁶ in which the electrochemical intercalation of the compounds $(\text{PbS})_{1.18}\text{TiS}_2$ and $(\text{PbS})_{1.18}(\text{TiS}_2)_2$ with silver was examined. It was demonstrated that the insertion of silver into the structure $(\text{PbS})_{1.18}\text{TiS}_2$ resulted in disproportionation of the latter into $\text{Ag}_x(\text{PbS})_{1.18}(\text{TiS}_2)_2$ and PbS .

Similar results were obtained upon intercalation of iron and nickel into layered misfit structures based on TiS_2 and LaS or CeS.⁷⁷ Monolayer intercalates could not be prepared, whereas the bilayer structures of the $A_n(\text{LaS})_{1.18}(\text{TiS}_2)_2$ type were synthesised and studied. Presumably, the formation of intercalates (in the case

of a comparable donor ability of the intercalant) becomes easier as the charge transfer from MX to TX₂ decreases and as the electron ‘capacitance’ of the unoccupied band is increased. In this respect, the probability of intercalation of layered misfit compounds possessing the 1T structure is higher than that of compounds with the 2H structure because a metal atom with octahedral coordination can accept a larger number of electrons than an atom with trigonal-prismatic coordination.

Intercalation of metals into the synthetic matrix Ta_{1-x}Re_xSe₂ was also studied.^{78,79} The electronic structure of this matrix can be changed by varying its composition, *i.e.*, by varying the *x* value. For *x* = 0.5, this matrix is isoelectronic and isostructural to the matrix 2H-MoSe₂, *viz.*, the *d*_{z²} band in this matrix is filled and intercalation is accompanied by disproportionation of the layered structure.

The results of a study⁴⁶ in which the possibility of the replacement of a portion of lanthanum atoms in (LaS)_{1+x}CrS₂ by ‘inert’ Sr was examined can be cited as supporting evidence for the above concept of electronic stabilisation. The results obtained demonstrated that the structure (LaS)_{1+x}CrS₂ contains a substantial amount (~0.2) of lanthanum vacancies, *i.e.*, the corresponding suprastructure is a nanocomposite. This fact was indirectly confirmed by the results of another study,¹⁶ where it was attempted to obtain images of LaS layers in the suprastructure (LaS)_{1.14}NbS₂ by scanning tunnelling electron and atomic-force microscopy; however, the attempts were unsuccessful.

Probably, the differences in the morphology of the synthesised crystalline species (BiS)_{1+x}(NbS)_{*m*} are also associated with the conditions of the interaction between the constituent substructures. Among the specimens obtained, layered structures as well as structures of the ‘insulation-tape bundle’ type were found. As mentioned above, no noticeable electron density transfer was observed in layered misfit structures with M = Bi or Sb, unlike those with M = Ln. In the case of the former structures, single crystals are deformed and take the shape of an ‘insulation-tape bundle’ or a bent tube (because stresses due to the incommensurability of the layers in one direction result in the curvature) due to the incommensurability of the intercalant MS and the nonrigidity of the TS₂ matrix.^{80–82} The optimum inner and outer radii of ‘bundles’ are determined by the force balance retaining the matrix rigidity as well as by the conditions of the interaction between substructures.

Unfortunately, data on the thermodynamic properties of layered misfit structures are lacking in the literature. We suggested that the formation of defects (discontinuities) in intergrowth incommensurate substructures and the degree of additivity of the substructure contributions to the observed properties of the suprastructure can be studied by thermal analysis and differential scanning calorimetry.

We established that the specific heats of the compounds (SnS)_{1+x}TaS₂ and (PbS)_{1+x}TaS₂ cannot be described in the context of the additivity. Anomalies were also found for the temperature dependence of the specific heat due to first-order phase transition. Thus it was demonstrated that compounds with the nonextreme stoichiometry (*x* = 0) did not give a low-temperature (35–70 °C) specific-heat peak, whereas these peaks for quenched and nonquenched samples of (SnS)_{1.15}TaS₂ differ in height. For all compounds based on TaS₂, the specific-heat peak was observed at 350 °C. The peak height depends on the stoichiometry and the conditions of cooling of the samples. Probably, these effects are associated with disruptions in one of the sublattices.

Our studies demonstrated that the compounds (SnS)_{1+x}TaS₂ actively decomposed at above ~600 °C in an inert atmosphere to liberate elementary sulfur. Apparently, the intercalates Sn_{*x*}TaS₂ were the final decomposition products. In the future, we hope to confirm the fact that the observed phase transitions are associated with discontinuities in one of the sublattices (MX). In our opinion, these compounds are thermodynamically unstable due to the effect of the incommensurability on the crystal structure. Appa-

rently, strengthening of the interaction between substructures (for a given incommensurability) leads to an increase in the instability of the suprastructure due to a change in the energy of the bonds between the metal and chalcogen atoms in one of the substructures.

We have presented sufficiently convincing evidence for the possibility of fragmentation of one of the sublattices in the misfit structure (MX)_{1+x}(TS₂)_{*m*}. The equation of motion was solved within the framework of the Frenkel–Kontorova model taking into account the anharmonicity of the elastic sublattice and the incommensurability between the period of this sublattice and the corresponding lattice parameter of the crystal environment. The corrections for the known solutions of the equation of motion in the harmonic approximation were also found. It was demonstrated that under conditions of anharmonicity of the interaction between the sublattice and the host lattice, two reasons for its possible fragmentation into particles of finite length exist, *viz.*, the incommensurability and doubling of the period of solutions of the nonlinear problem describing this model. The solution obtained determines the conditions of formation of one-dimensional nanocomposite structures and the limiting parameters at which the suprastructure of the ensemble changes from regular to random.

V. Conclusion

Incommensurate suprastructures, which have been studied thus far, are limited only to compounds in which one lattice parameter of intergrowth substructures is incommensurate (a one-dimensional case). Apparently, eutectics can serve as abundant examples of suprastructures characterised by incommensurability along all three crystallographic directions. As it usually is, the transformation from a one-dimensional model to a three-dimensional system, presents problems. However, it can be said that some general criteria for the formation of suprastructures with the three-dimensional incommensurability were revealed.

First, it is apparent that the incommensurability of intergrowth substructures in real suprastructures occurs within particular limits. Apparently, for some incommensurability parameters, the interaction between sublattices can lead to the formation of defects of different types, including fragmentation of one of the substructures. We failed to find literature data on the dependence of the properties and structures of layered misfit structures on the incommensurability. However, it is apparent that the character of the interaction between substructures should depend on the stoichiometric ratio, *i.e.*, on the *x* and *m* values. As mentioned above, indirect evidence is available for the fact that monolayer structures undergo disproportionation to form bilayer and simple structures as the *x* parameter changes (see the data on intercalation of misfit structures^{14,76,77}). Other data (tubular morphology of particles,¹⁵ the results of studies by scanning tunnelling electron and atomic-force microscopy⁷⁰ and results of our investigations of thermodynamic properties of misfit structures) indicate that defects in substructures comprising the misfit structure or in one of these substructures are frequently observed.

Second, it was proved that it is important to meet the conditions of electronic stabilisation of suprastructures. Since the charge transfer is the major mechanism responsible for the interaction between structural elements in misfit suprastructures, the conditions of electronic stabilisation determine both the stabilities of substructures and the existence of a suprastructure as a whole. The above-considered differences in the character of the interaction between substructures MX and TX₂ determine both the possibility of formation of defects in the substructures and their character [see the data^{44,45,69} on the structures (LaS)_{1+x}CrS₂, (LaSe)_{1+x}VSe₂ and (PbS)_{1+x}TiS₂]. The differences in the morphology of misfit particles are also attributable to these facts.¹⁵

Third, it was established that the nonrigidity of substructures is of importance, at least it was demonstrated that deformations of sublattices due to their incommensurability should be taken into

account both in structural studies and in investigations of physicochemical properties of incommensurate compounds. For example, it can be suggested that bonds in one sublattice can be cleaved at particular tensile stresses and new bonds in another sublattice can be formed at particular compression stresses. The latter possibility is supported by the results of the study of the structures $(\text{BiS})_{1.08}\text{TaS}_2$ and $(\text{BiSe})_{1.09}\text{TaSe}_2$ ¹⁵ in which short (as in metals) Bi–Bi bonds were found. The results of the study¹⁶ provided indirect evidence for the cleavage of bonds in MX substructures.

Finally, approaches and procedures, which allow one to determine the conditions of fragmentation of substructures, were theoretically justified.

In the present review, we call attention to some apparent relationships responsible for the structural characteristics, structure imperfection and morphology of particles of crystalline suprastructures formed from incommensurate elements. Although it is evident that this problem is of importance in solid-state chemistry and in many fields of materials science, it has not been discussed previously in the literature.

Evidently, three situations can occur upon formation of incommensurate intergrowth suprastructures. In the first case, the nonrigidity of the lattices compensates for their insignificant incommensurability. In this case, the formation of a suprastructure is accompanied by stresses, but it does not disturb the stoichiometry. In the second situation, rigid substructures exist and the interaction between these substructures are rather weak. In this case, rather well-organised crystalline suprastructures are formed at any incommensurability. Their limiting stoichiometry is determined by the incommensurability, and the properties, most likely, additively depend on the properties of the constituent elements. The third situation is associated with mechanisms of structural compensation. Due to the strong interaction between substructures, their nonrigidity and substantial incommensurability, discontinuities can appear in one of the sublattices accompanied by the formation of nanocomposites. The structural compensation of the resulting stresses may lead to the formation of unusual defects or give rise to an unusual morphology of particles of suprastructural aggregates. It is also possible that particular limitations on the particle sizes occur. The last-mentioned situation is based on rather abundant experimental data. In our opinion, this situation is of prime interest within the framework of the problems under consideration.

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^b — *Russ. J. Inorg. Chem. (Engl. Transl.)*

Some new aspects in the application of perfluoroalkyl halides in the synthesis of fluorine-containing organic compounds

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Abstract. The approaches to the activation of perfluoroalkyl halides used as intermediates in the synthesis of partially fluorinated compounds are considered. The conditions for reactions of organic compounds with perfluoroalkyl iodides in the presence of reductants ($\text{Na}_2\text{S}_2\text{O}_4$, $\text{HOCH}_2\text{SO}_2\text{Na}$), metals and metal salts, redox systems ($\text{Na}_2\text{S}_2\text{O}_8$, Bu^tOOH , $\text{Pb}(\text{OAc})_4$, H_2O_2 – FeSO_4 , $\text{Ce}(\text{SO}_4)_2$) and transition metal complexes are described. The generation of perfluoroalkyl radicals by a single-electron transfer mechanism are discussed. The introduction of perfluoroalkyl groups into aromatic and unsaturated organic compounds and functionalisation of perfluoroalkyl iodides, particularly, their transformation into perfluoroalkanesulfinic and perfluoroalkane-carboxylic acids and aldehydes, are considered. The bibliography includes 442 references.

I. Introduction

The introduction of fluorine atoms into the molecules of organic compounds not only changes their physical and chemical properties but also forms the basis for the development of new synthetic procedures, sometimes unusual for organic chemistry, for the generation of C–C bonds and cyclic systems.^{1–6}

Partially fluorinated organic compounds, particularly those containing perfluoroalkyl groups, find wide application in the synthesis of novel materials, in the design of medicinal and agricultural preparations and in different branches of technology.^{7–24} This, in turn, stimulates the development of novel, and the perfection of the existing methods for the introduction of polyfluorinated fragments into organic substrates. The interest of investigators in the possibility of direct introduction of such fragments into organic molecules is determined by diverse applicability of fluorine-containing compounds and unique physical and biological properties imparted to these compounds by fluorine, because regioselective substitution of a perfluoroalkyl group for the hydrogen atom in aromatic or heterocyclic systems may significantly influence their properties.

The introduction of perfluoroalkyl groups, in the first place, of CF_3 , into organic molecules is based on three main types of chemical transformations, viz., those involving electrophilic (see, e.g., Refs 2, 25, 26), nucleophilic²⁷ and radical^{28–30} species. Thus, the availability of perfluoroalkyl iodides and the feasibility of their use in the synthesis of organometallic compounds made it possible to develop novel procedures for the generation of perfluoroalkyl radicals and to study their reactions.^{28–30}

The addition of perfluoroalkyl halides to alkenes and alkynes is one of the most fundamental procedures for introducing perfluoroalkyl groups into the molecules of organic substrates. Perfluoroalkyl radicals are traditionally generated photochemically,^{31–41} thermally⁴² or electrolytically,^{43,44} viz., by:

(i) photolysis or thermolysis of perfluoroalkyl halides, perfluoroalkanesulfonyl chlorides and organometallic compounds containing perfluoroalkyl substituents;^{45–50}

(ii) decomposition of polyfluorinated acyl peroxides of the general formula $(\text{C}_n\text{F}_{2n+1}\text{COO})_2$ ^{51–64} and electrolysis of perfluoroalkane-carboxylic acids.^{65–69}

These methods have successfully been used in the perfluoroalkylation of alkenes, aromatic, natural and heterocyclic compounds. Their advantages and disadvantages have been described in detail.^{45,65–68} To the main disadvantages of these methods one may relate the difficulty in their implementation under conditions of large-scale manufacture, low selectivity and low yields of the target products. Moreover, the preparation of the starting building blocks, which are often toxic and expensive, demands special conditions.¹⁹ These circumstances together have made it necessary to develop efficient methods for introducing perfluoroalkyl groups† into organic molecules. The main emphasis in these studies was laid on their direct incorporation by *in situ* generation of perfluoroalkyl radicals. This, in turn, required simple, available and inexpensive reagents and simplification of the procedure of direct introduction of perfluoroalkyl groups into organic molecules.

This search culminated in the development of novel approaches to the generation of perfluoroalkyl radicals from perfluoroalkyl halides in reactions occurring by a single-electron transfer mechanism. A variety of initiators for such reactions are currently known. The ease of performance and high efficiency of the perfluoroalkylation reaction as well as high accessibility of the reagents leave hope that this reaction will be very efficient in the synthesis of fluoroorganic compounds. The present work is an overview of the published data concerning perfluoroalkylation

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† The electrophilic nature of the perfluoroalkyl radical was reported by Baum *et al.*⁷⁰

reactions, it highlights the key events in the methodology of introduction of perfluoroalkyl groups into organic compounds.

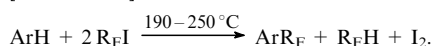
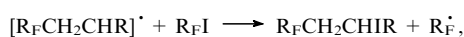
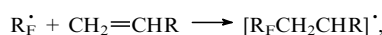
II. The use of perfluoroalkyl halides in the synthesis of partially fluorinated compounds

Perfluoroalkyl iodides and bromides have recently received considerable attention owing to their accessibility, high reactivity and ability to be used in perfluoroalkylation reactions, including new ones.

These reactions can be initiated in various ways, *viz.*, thermally,^{42,71–74} electrochemically,^{43,44} photolytically,^{31–41,75,76} or in the presence of free radical inducers, *e.g.*, hydrogen peroxide,⁷⁷ α,α -azobis(dimethylpentanonitrile),^{78–80} α,α -azobis(cyclohexanecarbonitrile)⁸¹ and α,α -azobis(isobutyronitrile) (AIBN).^{79–85} By selecting appropriate reaction conditions (*viz.*, solvent, temperature, reaction time), one may carry out perfluoroalkylation of various organic compounds.

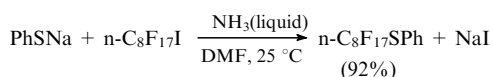
These reactions are accompanied by the cleavage of C–I and C–Br bonds, but not of C–F bonds because the latter possess greater strength. Under certain conditions, perfluoroalkyl halides act as radical reagents, which perfluoroalkylate unsaturated organic compounds. This approach was repeatedly used in the chemistry of fluoroorganic compounds.^{36,86–93}

Perfluoroalkyl iodides (R_F-I) are widely used as a source of perfluoroalkyl radicals, their addition to alkenes⁴⁶ and reactions with aromatic hydrocarbons under thermolysis conditions have been described, *e.g.*:



1. Reactions of perfluoroalkyl iodides with organic substrates in the presence of nucleophilic agents

This methodology was first used^{94–102} in reactions of alkene- and arene-thiols with perfluoroalkyl iodides in liquid ammonia upon UV-irradiation. The corresponding aryl perfluoroalkyl sulfides were isolated in high yields.



Reactions with perfluoroalkyl bromides and diiodoperfluoroalkanes were conducted in a similar way, this was further extended to selenium and tellurium derivatives and representatives of other classes.^{103–108}

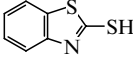
Later, it was shown that reactions of perfluoroalkyl iodides with trialkylammonium and sodium salts of benzenethiols (Table 1)¹⁰² or sodium benzothiazole-2-thiolate^{108,109} do not always require UV-irradiation. These reactions may occur in bipolar aprotic solvents at room temperature and are characterised by high yields.

$R-\text{C}_6\text{H}_4-\text{SH} + R_FI \xrightarrow{NaH} R-\text{C}_6\text{H}_4-SR_F$			$R-\text{C}_6\text{H}_4-\text{SH} + R_FI \xrightarrow{NaH} R-\text{C}_6\text{H}_4-SR_F$		
R	R_F	Yield (%)	R	R_F	Yield (%)
H	C_4F_9	66	NO_2	C_6F_{13}	93
Me	C_4F_9	77	NO_2	C_8F_{17}	93
OH	C_4F_9	30	NO_2	$C_4F_9(CH_2)_2$	90
Cl	C_4F_9	83	NO_2	$C_6F_{13}(CH_2)_2$	68
NO_2	C_4F_9	99			

Alkali metal benzenethiolates are convenient reagents, but in this case substitution reactions occur only on irradiation.^{110–112} Nitrobenzene can be used as an initiator of this reaction. For example, the reactions of perfluorohexyl bromide with potassium

Table 1. Reactions of perfluoroalkyl iodides with triethylammonium arenethiolates.¹⁰²

$$ArS^-NH_4^+ + R_FI \xrightarrow{Et_3N} ArSR_F + ArSSAr$$

Ar	Reaction conditions			Yield (%)		
	solvent	$T/^\circ C$	t/h	A	B	other products
Ph	DMF	19–20	2	83	3	—
4-MeO ₂ CNHC ₆ H ₄	DMF	0–5	3	17	12	30
	DMF	0–22	5	30	7	54
	MeCN	21–22	0.5	98	traces	—
		21–22	2	82	2	—
	THF	21–22	1.5	64	10	—
2-NH ₂ C ₆ H ₄	HMPA ^a	21–22	3	75	3	—
	MeCN	21–30	0.5	84	—	—
4-MeOC ₆ H ₄	DMF	23–24	1.5	66	7	—
	MeCN	22–40	2	88	6	—
4-ClC ₆ H ₄	DMF	22	2	72	3	—
	MeCN	21–22	4	40	12	9
4-HO ₂ CC ₆ H ₄	DMF	22–30	0.5	72	traces	traces
4-MeO ₂ CC ₆ H ₄	DMF	20	3	39	13	—
4-NO ₂ C ₆ H ₄	DMF	50–55	5	traces	6	80
	DMF	20–22	48	traces	traces	87
	DMF	20–22	120	58.8	—	20
	DMF	20–22	24	72.2	3.8	—

^a HMPA is hexamethylphosphoramide.

benzenethiolates in DMF in the presence of nitrobenzene result in aryl perfluorohexyl sulfides.¹¹³

$$ArSK + R_FBr \xrightarrow{PhNO_2} ArSR_F$$

Ar	R_F	Yield (%)	Ar	R_F	Yield (%)
Ph	C_2F_5	33	4-MeOC ₆ H ₄	CF_3	83
Ph	$n-C_6F_{13}$	72	3-MeOC ₆ H ₄	CF_3	40
4-MeC ₆ H ₄	CF_3	75	3-NH ₂ C ₆ H ₄	CF_3	23
4-MeC ₆ H ₄	$n-C_6F_{13}$	77	4-ClC ₆ H ₄	CF_3	34
Ph	CF_3	45	4-CF ₃ C ₆ H ₄	CF_3	13

The reaction of $CF_3(CF_2)_9I$ with sodium 4-fluorobenzene-thiolate in DMF at 30–45 °C gives 4-FC₆H₄S(CF₂)₉CF₃ (yield 94%).¹¹⁴ On the other hand, benzenethiol,^{115,116} benzeneselenol^{117–119} and benzenetellurol^{120,121} anions, which are known to be strong nucleophiles, generate the corresponding perfluoroalkyl radicals from perfluoroalkyl iodides introduced into the reaction with alkenes. In this way, efficient perfluoroalkylselenylation (Table 2)^{117–119} and perfluoroalkyltellurylation (Table 3)^{120,121} of a series of alkenes were carried out.

In $PhSeNa - R_FX$ and $PhTeNa - R_FI$ systems, perfluoroalkyl radicals are generated from perfluoroalkyl halides at room temperature. This property was used in the development of a new approach to the generation of perfluoroalkyl radicals at low temperatures.

The yields of perfluoroalkyl phenyl sulfides (R_FSPh) depend on the length of the alkyl chain. In the case of $C_nF_{2n+1}I$, where $n = 4, 6$ and 8 , the yields are 78%, 84% and 86%, respectively. Perfluoroalkyl radicals add to the multiple bond regioselectively.¹

A procedure for the synthesis of aryl perfluoroalkyl sulfides from perfluoroalkyl halides and benzenethiols was proposed by

Table 2. Perfluoroalkylselenenylation of alkenes.^{117–119}

$$R^1-CH=CH-R^2 \xrightarrow{PhSeNa-R_FX} \begin{matrix} R^1 & & R_F \\ & \diagdown & / \\ & C & C \\ & / & \diagdown \\ PhSe & & R^2 \end{matrix} + R_FSePh + (PhSe)_2$$

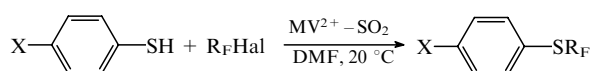
Alkene	R _F X	Yield (%)		
		A	R _F SePh	(PhSe) ₂
	C ₈ F ₁₇ I	63	25	15
	C ₆ F ₁₃ I	55	20	19
	C ₈ F ₁₇ I	59	19	21
	C ₆ F ₁₃ I	57	17	13
	CF ₃ Br	26	34	31
	C ₈ F ₁₇ I	86	7	traces
	C ₆ F ₁₃ I	84	6	
	CF ₃ Br	38	32	20
	C ₈ F ₁₇ I	66	traces	30
	C ₈ F ₁₇ I	15	60	17
	C ₈ F ₁₇ I	39	42	9

Table 3. Perfluoroalkyltellurylation of alkenes.^{120, 121}

$$R-CH=CH_2 \xrightarrow{PhTeNa-R_FX} \begin{matrix} TePh \\ | \\ R-CH-CH_2-R_F \end{matrix}$$

Alkene	Yields for different R _F X (%)		
	CF ₃ Br	C ₄ F ₉ I	C ₈ F ₁₇ I
	57	81	59
	44	58	39
CH ₂ =CH ₂	44	63	47
	30	64	54

Koshechko *et al.*¹⁰⁵ who used MV²⁺–SO₂ (MV²⁺ is methylviologen, *N,N'*-dimethyl-4,4'-bipyridinium salt) and I₂–SO₂ systems as electron carriers.



R_F = CF₃, Hal = I: X = H (91.2%), NHCO₂Me (88.5%), Cl (53%), NO₂ (9.2%);¹⁰⁴

R_F = CF₃, Hal = Br: X = H (74%), Me (41%);¹⁰⁵

R_F = CFCl₂CF₂, Hal = Cl, X = H (34%);¹⁰⁵

R_F = CF₃, Hal = Br: X = NHCO₂Me (94%), H (78%), Br (64%), Cl (60%), NO₂ (24%) (reaction with benzenethiols).¹⁰⁷

This reaction was studied in detail using spectrophotometry and cyclic voltamperometry¹⁰⁵ and provided conclusive evidence for the intermediate formation of the 'CF₃ radical. Kinetic studies revealed that this reaction is of the second order with respect to the reagents, *i.e.*, $v = k_2[ArSH][MV^{2+}2I^-]$. The k_2 values for PhSH and 4-MeC₆H₄SH were equal to 4.6 and 7.1 litre mol⁻¹ s⁻¹, respectively, at 30 °C.

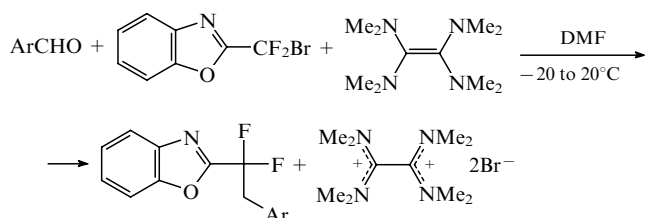
After addition of SO₂ to the system, the reaction is controlled by the radical anion SO₂^{•-} generated from SO₂ by the radical

cation MV^{•+}, which, in turn, is generated upon action of ArS⁻ on MV²⁺. The interaction of the intermediate radical anion [CF₃SPh]^{•-} with MV²⁺ gives the reaction product and MV^{•+}.

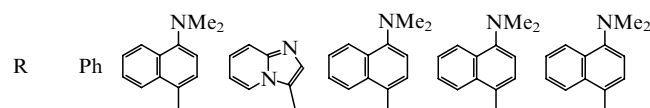
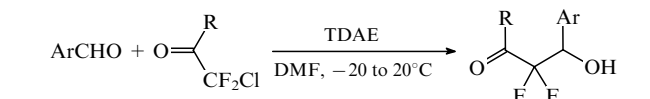
It is noteworthy that SO₂ is an efficient electron carrier in the electrochemical cathode trifluoromethylation of benzenethiols with trifluoromethyl bromide.^{106, 107}

Tetrakis(dimethylamino)ethylene (TDAE) proved to be an efficient reductant initiating the cleavage of C–I and C–Br bonds in reactions with unsaturated compounds. Thus TDAE forms a complex (*e.g.*, with CF₃I), which can act as a nucleophilic trifluoromethylating agent in polar solvents. The ionisation potential of TDAE is equal to 6.13 eV,¹²² being close to that of zinc, which is known to be a potent reductant [the standard electrode potential (E°) of zinc is –0.763 V]. TDAE is also known to be a very potent electron donor; its ionisation energy (591 kJ mol⁻¹) is lower than that of zinc (906 kJ mol⁻¹) and is close to that for lithium (521 kJ mol⁻¹). Electrochemical oxidation of TDAE in acetonitrile occurs in two reversible single-electron steps and results in [TDAE]^{•+} and [TDAE]²⁺ ($E^\circ = -0.78$ and -0.61 V, respectively).¹²³

Later, this methodology was used in the synthesis of dialkyl-(trifluoromethyl)amines by the reaction of CF₂Br₂ with secondary amines in the presence of TDAE¹²⁴ and in reactions of 2-(bromodifluoromethyl)benzoxazole¹²⁵ and chlorodifluoromethyl ketones with aromatic aldehydes in the presence of TDAE.¹²⁶



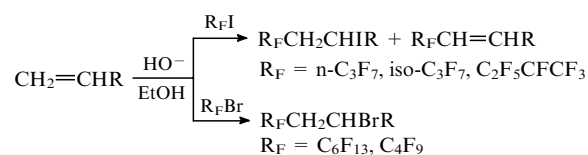
Ar	Ph	4-FC ₆ H ₄	4-PhC ₆ H ₄	4-CF ₃ C ₆ H ₄	4-CNC ₆ H ₄
Yield (%)	62	67	45	63	61



Ar	Ph	Ph	Ph	4-CF ₃ C ₆ H ₄	4-FC ₆ H ₄	
Yield (%)	55	45	55	58	55	57

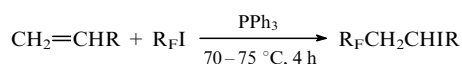
The acyldifluoromethyl anion generated from chlorodifluoromethyl ketone reacts with aromatic aldehydes to give the corresponding hydroxy ketones containing a CF₂ fragment in the α-position.¹²⁶

In the presence of alcoholates, perfluoroalkyl iodides and -bromides react with alkenes to yield the addition products.^{127–131} This suggests that alcoholates, as is the case with the Cannizzaro reaction with aldehydes, act as reducing agents rather than induce splitting of perfluoroalkyl halides by the haloformic pathway.



R = n-C₃H₁₁, CH₂OH.

Phosphines [PPh₃, PBu₃ⁿ, P(NEt₂)₃, P(OEt)₃] are used as activators in the reaction of perfluoroalkyl iodides with alkenes.^{132–145}

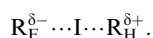


R = n-C₄H₉, n-C₆H₁₃.

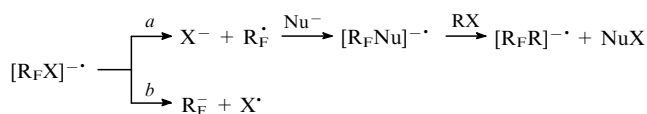
R _F	Yield (%)	R _F	Yield (%)
C ₆ F ₁₃	79	C ₈ F ₁₇	72
Cl(CF ₂) ₄	81	FSO ₂ (CF ₂) ₂ O(CF ₂) ₂	28
Cl(CF ₂) ₆	83	FSO ₂ (CF ₂) ₂ O(CF ₂) ₈	87

In the presence of P(NEt₂)₃, perfluoroalkyl iodides R(CF₂)_nI (R = CF₃, n = 4–7) react with alkenes¹⁴⁰ or benzoyl chloride derivatives¹⁴¹ with the formation of addition products at the multiple bond and the corresponding ketones (yields 32%–43%). The hexamethyldisiloxane–sodium methoxide system in THF is also effective to this goal.¹⁴²

The reaction of perfluoroalkyl iodides with nucleophiles manifests the features of a S_{RN}1 reaction^{44, 146} and proceeds smoothly under relatively mild conditions. The stereochemistry of the reaction of perfluoroalkyl iodides with alkenes suggests that it is the perfluoroalkyl radical that initially attacks the alkene. Presumably, the initiation consists in electron transfer from the nucleophile to the perfluoroalkyl iodide resulting in the generation of the radical anion [R_FI]^{•−};^{147, 148} the process is exothermic. The radical anion formed must be rapidly decomposed into the perfluoroalkyl radical and the iodide ion. The efficiency of the free-radical chain growth in the reaction with alkenes is provided under conditions such that the decomposition of the radical anion [R_FI]^{•−} is a fast reaction; apparently, the polar effect in the translocation of the iodine favours the decomposition:



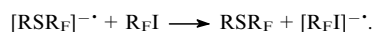
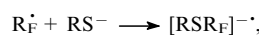
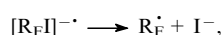
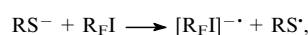
The radical anion [CF₃I]^{•−} has been detected in a solid state as a stable species at 77 K. At 100 K, it dissociates into the trifluoromethyl radical and the iodide ion.^{149–155} The reaction of the perfluoroalkyl radical with an anionic substrate generates a radical anion which further reacts with perfluoroalkyl iodide to give [R_FI]^{•−} according to the S_{RN}1 mechanism.^{152–155} A more detailed description of these reactions is given in Refs 116, 156–160. Further transformations of the radical anion [R_FX]^{•−} may proceed in two pathways (routes *a* and *b*), which depends on thermodynamic factors.



Nu is nucleophile.

It was shown⁴⁷ that the R_F• and I• fragments (but not the radical anions [R_FI]^{•−}) are formed in polar solvents. Hence a question arises about the pathways of generation of the radical R_F•. It is quite probable that only the C–I bonds are involved in the formation of donor–acceptor complexes with perfluoroalkyl iodides, which favours the manifestation of electrophilic properties of R_FI in solvents of the hexamethylphosphoramide (HMPA) and DMF type. Presumably, the translocation of the radical anion centre to R_FI followed by the generation of the R_F• radical is the limiting step in this reaction.

The formation of radicals from perfluoroalkyl halides by the S_{RN}1 mechanism is one of the most characteristic features of electron transfer reactions in organic chemistry.¹⁶¹ The S_{RN}1 mechanism is especially favourable for perfluoroalkyl halides, since the latter manifest very low activity in nucleophilic reactions of the S_N1 and S_N2 type. Studies of perfluoroalkyl halides reactions occurring *via* the S_{RN}1 mechanism were begun in the 1970's.^{162–170}



The values of the radical formation energy (*E*) in the gas phase were found to be as follows:⁸⁹

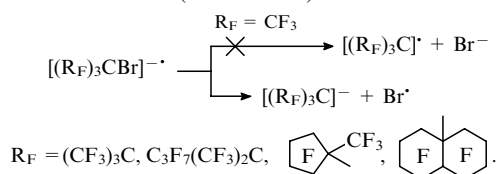
Radical	<i>E</i> / eV	Radical	<i>E</i> / eV
•CF ₃	2.10	F•	3.39
CF ₃ •CF ₂	2.10	Cl•	3.61
(CF ₃) ₂ •CF	2.65	Br•	3.37
(CF ₃) ₃ C•	3.40	I•	3.06

Therefore, route *a* in the transformation of radical anions is probable for compounds CF₃X, C₂F₅X, (CF₃)₂CFX (but not for X = I), while route *b* is probable for (CF₃)₃CX (at all values of X) and R. The direction of a reaction in solution depends on the value of free energy of solvation (Δ*G*). For example, in water Δ*G* has the following values:

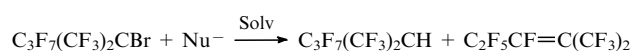
Anion	Δ <i>G</i> / kJ mol ^{−1}	Anion	Δ <i>G</i> / kJ mol ^{−1}
F [−]	−472	I [−]	−283
Cl [−]	−347	R _F [−]	−200
Br [−]	−321		

In this case, route *a* seems to be preferable for all R_FX [probably, with the exception of (CF₃)₃CCl] and, perhaps, (CF₃)₂CFI.

The transfer of electrons from the charged nucleophile to Bu⁺Br leads to the formation of a radical anion–radical pair; its further transformations differ from those for an analogous pair in the case of R_FBr, which is decomposed by the route *b*, resulting in the radical anion [R_FX]^{•−}. Quantum-chemical calculations using the AM1 method revealed that the formation of the radical anion generating the ternary perfluoroalkyl carbanion (CF₃)₃C[−] and the radical Br• (see Refs 146, 165) is due to higher electronegativity of the tertiary group of the perfluoroalkyl radical. The enthalpy of formation of this anion and the Br• radical (Δ*H*₁) is 17.6 kcal mol^{−1}, whereas that of the tertiary perfluoroalkyl radical and the bromide ion (Δ*H*₂) is much higher, *i.e.*, 57.9 kcal mol^{−1} (see Ref. 166).



The occurrence of this reaction through the formation of a radical anion was confirmed experimentally.¹⁶⁶ The reactions of (R_F)₃CBr with nucleophiles, *e.g.*, Na₂S, NaSH, KSCN, KCN, R₄NX (X = Cl, Br, I), in organic solvents (*e.g.*, MeCN, DMF, CH₂Cl₂, EtOAc) result in the quantitative formation of mixtures of (R_F)₃CH and perfluoroalkene. This can be attributed to the reaction of the perfluoroalkyl halide with the proton from the medium as well as to stabilisation of the perfluoroalkyl carbanion due to elimination of the fluorine anion from the CF₂ fragment in the α-position.



Nu is nucleophile, Solv is solvent.

The electron transfer from the reductant to perfluoroalkyl halide resulting in the formation of the corresponding radical anions is highly efficient, since free σ*-orbitals of the C–Hal bonds (Hal = Cl, Br, I) lie fairly low on the energy axis. Active generation of such radical anions requires a reductant the standard reduction potential (*E*_{red}^o) of which is higher than that of the

alkyl halide involved in the reaction. Depending on the structure of the alkyl fragment and the nature of the halogen, the reducing potentials ($E_{1/2}$ relative to SCE) of perfluoroalkyl halides (Pt electrode in MeCN) vary from -1.10 to $+0.71$ V.¹⁷¹

R _F Hal	$E_{1/2}$ /V	R _F Hal	$E_{1/2}$ /V
CF ₃ I	-1.10	(CF ₃) ₃ CBr	-0.14
C ₃ F ₇ I	-1.00	C ₃ F ₇ CBr(CF ₃) ₂	-0.09
I(CF ₂) ₄ I	-0.96	1-bromo-1-methylperfluoro-	0.12
(CF ₃) ₂ CFI	-0.66	cyclopentane	
cyclo-C ₆ F ₁₁ I	-0.36	1-bromoperfluorobicyclo-	0.71
I ₂	0.10	[4.4.0]decane	
(CF ₃) ₃ CI	0.14	1-chloro-1-methylperfluoro-	-1.02
C ₃ F ₇ CI(CF ₃) ₂	0.32	cyclopentane	
C ₃ F ₇ CCl(CF ₃) ₂	-0.97	1-chloroperfluorobicyclo-	-0.95
(CF ₃) ₂ CFBr	-1.05	[4.4.0]decane	

Consequently, the presence in the reaction mixture of a compound with a higher (in comparison with perfluoroalkyl halide) value of E_{red}° makes possible the generation of the radical anion $[\text{R}_F\text{X}]^{\cdot-}$; its decomposition results in the perfluoroalkyl radical. The latter can be further involved in reactions with organic compounds. In the subsequent sections, this process will be exemplified with both classical reductants and redox systems.

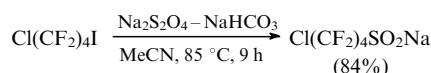
2. Sulfinylation of perfluoroalkyl iodides

The addition of perfluoroalkyl halides to the C=C bond of alkenes is the most promising approach to the generation of C—C bonds in the synthesis of polyfluorinated compounds. Numerous synthetic procedures for perfluoroalkylation of alkenes, especially by R_FI, have been developed. One of them includes thermal or photochemical induction of free-radical reactions.

This approach was developed by a group of Chinese investigators who studied sulfinate dehalogenation of halogen-containing hydrocarbons. Thus it was demonstrated for the first time^{54, 172–177} that perfluoroalkyl iodides react with sodium dithionite (Na₂S₂O₄) to yield sulfinic acid derivatives. The chemistry of perfluoroalkanesulfonates including their synthesis, properties, reactions and applications is described in the reviews (see Refs 158–160).

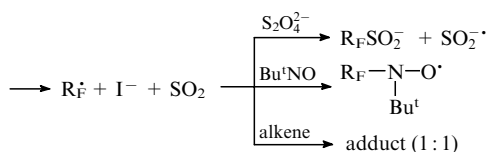
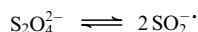
The inexpensive reducing agent Na₂S₂O₄ can be used for the preparation of perfluoroalkanesulfinic acid salts from perfluoroalkyl halides (R_FX, where X = Br, I, or R_FCCl₃) under relatively mild conditions. This method is widely employed in reactions of these salts with alkenes, dienes, alkynes and aromatic compounds. On the other hand, this system is efficient mostly for polyfluorinated alkyl halides.¹⁷² Bromine and iodine atoms in the perfluori-

nated carbon chain are easily substituted and the target product is formed in a high yield. More recent studies confirmed the efficacy of this approach.^{178–192}



Later, it was found that other nucleophilic sulfur derivatives also react with perfluoroalkyl iodides to give salts of perfluoroalkanesulfinic acid (Table 4).^{22, 143, 144, 184}

Presumably, these reactions occur *via* a single-electron transfer (SET) mechanism as can be evidenced from the trapping of perfluoroalkyl radicals by alkenes and nitroso compounds.⁵⁴



The sulfonylation with sodium dithionite gives an access to perfluoroalkanesulfonic acids, which are valuable intermediates in the synthesis of surfactants, without recourse to electrochemical fluorination and using accessible perfluoroalkyl iodides.^{134, 173, 184, 185, 193} For example, I(CF₂)₂O(CF₂)₂SO₃Na can be prepared from I(CF₂)₂O(CF₂)₂I using phase-transfer catalysis in polyethylene glycols-200 and -600 or in acetonitrile, ethanol or diglyme.

Perfluoroalkyl bromides also react with sodium dithionite.^{172–176, 194, 195} Thus, CF₃Br gives sodium trifluoromethanesulfinate in 90% yield, and sulfinylation products are formed from 1,1,1-trichloroperfluoroalkanes in yields of 90% and higher.



R = Cl, F, CF₃, Cl(CF₂)₂, Cl(CF₂)₄, Cl(CF₂)₆.

The reactions of α,ω -diiodoperfluoroalkanes¹⁸³ and α,ω -dibromoperfluoroalkanes¹⁸⁹ with 1 or 2 equiv. of Na₂S₂O₄ in aqueous MeCN in the presence of sodium hydrogencarbonate result in sulfonates, *e.g.*, I(CF₂)₆SO₂Na and NaSO₂(CF₂)₆SO₂Na, which in turn give the corresponding sulfonyl chlorides, *e.g.*, I(CF₂)₆SO₂Cl and ClSO₂(CF₂)₆SO₂Cl ($n = 3, 4, 6$) upon chlorination at 0 °C (Table 5).

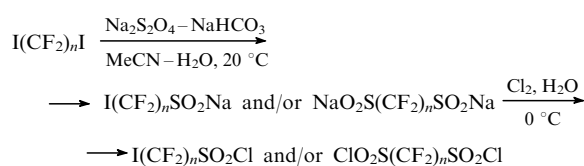
Table 4. Synthesis of sodium perfluoroalkanesulfonates.

Nucleophile	R _F X	Reaction conditions		Product	Yield (%)
		solvent	$T / ^\circ\text{C}$		
Na ₂ S ₂ O ₄	F(CF ₂) ₈ I	MeCN–H ₂ O	80–85	F(CF ₂) ₈ SO ₂ Na	95
	F(CF ₂) ₈ Br	MeCN–H ₂ O	20	F(CF ₂) ₈ SO ₂ Na	91
	CF ₃ CCl ₃	MeCN–H ₂ O	25	CF ₃ CCl ₂ SO ₂ Na	73
	I(CF ₂) ₂ O(CF ₂) ₂ CO ₂ Na	H ₂ O	85	NaSO ₂ (CF ₂) ₂ O(CF ₂) ₂ CO ₂ Na	96
HOCH ₂ SO ₂ Na	Cl(CF ₂) ₆ I	MeCN–H ₂ O	85	Cl(CF ₂) ₆ SO ₂ Na	65
	Cl(CF ₂) ₈ I	MeCN–H ₂ O	85	Cl(CF ₂) ₈ SO ₂ Na	75
NaHSO ₃ –K ₃ Fe(CN) ₆	Cl(CF ₂) ₈ I	DMF–H ₂ O	70–80	Cl(CF ₂) ₈ SO ₂ Na	88
NaHSO ₃ –FeCl ₃	F(CF ₂) ₆ I	DMF–H ₂ O	70	F(CF ₂) ₆ SO ₂ Na	63
Na ₂ S ₂ O ₅	Cl(CF ₂) ₄ I	DMF–H ₂ O	80	Cl(CF ₂) ₄ SO ₂ Na	85
	Cl(CF ₂) ₆ Br	DMF–H ₂ O	80	Cl(CF ₂) ₆ SO ₂ Na	79
NaHSO ₃	I(CF ₂) ₂ O(CF ₂) ₂ SO ₂ F	DMF–H ₂ O	70–80	NaSO ₂ (CF ₂) ₂ O(CF ₂) ₂ SO ₂ Na	95
	F(CF ₂) ₆ Br	DMF–H ₂ O	70–80	F(CF ₂) ₆ SO ₂ Na	90
K ₂ SO ₃	I(CF ₂) ₂ O(CF ₂) ₂ SO ₂ F	dioxane–H ₂ O	70	KSO ₂ (CF ₂) ₂ O(CF ₂) ₂ SO ₂ F	90

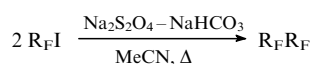
Table 5. Sulfonylation with subsequent chlorination of α,ω -diiodoperfluoroalkanes $\text{I}(\text{CF}_2)_n\text{I}$.^{183, 189}

<i>n</i>	$\text{I}(\text{CF}_2)_n\text{I}$: : $\text{Na}_2\text{S}_2\text{O}_4$ (see ^a)	MeCN : : H_2O (see ^a)	Product	Yield (%) ^b
3	1:1	10:3	$\text{I}(\text{CF}_2)_3\text{SO}_2\text{Cl}$	28 (80)
4	1:1	10:3	$\text{I}(\text{CF}_2)_4\text{SO}_2\text{Cl}$	25 (90)
6	1:1	20:3	$\text{I}(\text{CF}_2)_6\text{SO}_2\text{Cl}$	39 (84)
3	1:2	1:1	$\text{ClSO}_2(\text{CF}_2)_3\text{SO}_2\text{Cl}$	73 (100)
4	1:2	1:1	$\text{ClSO}_2(\text{CF}_2)_4\text{SO}_2\text{Cl}$	83 (100)
6	1:2	1:1	$\text{ClSO}_2(\text{CF}_2)_6\text{SO}_2\text{Cl}$	75 (> 95)

^a Molar ratio. ^b The figures in parentheses correspond to the yields according to ¹⁹F NMR spectroscopy data.



One should bear in mind that dimerisation of a perfluoroalkyl radical is also possible. For example, heating of perfluoroalkyl iodide in the presence of the $\text{Na}_2\text{S}_2\text{O}_4-\text{NaHCO}_3$ system in MeCN for 48 h gives a dimeric product.⁹³



The sulfinate dehalogenation reaction has opened up new opportunities for the synthesis of perfluoroalkanesulfinic and -sulfonic acids and their derivatives, since it permits direct transformation of perfluoroalkyl halide into perfluoroalkyl sulfinate and thus eliminates the necessity for the intermediate step, *i.e.*, the synthesis of an organometallic derivative. There is no doubt that this approach holds great promise for wide-scale technological application.^{172–175, 178–181, 189, 195}

III. Reactions of perfluoroalkyl halides with organic substrates occurring by a single-electron transfer mechanism

The addition of perfluoroalkyl iodides to alkenes and alkynes is one of the most important methods for the synthesis of commercially valuable fluorohydrocarbons used as intermediates in the preparation of novel materials and products.²⁰ In this Section, we shall consider a novel approach to the functionalisation of the accessible perfluoroalkyl iodides, which consists in the involvement of an intermediate perfluoroalkyl radical generated under the action of various initiators. This reaction is described by a well-known mechanism, $\text{S}_{\text{RN}}1$. The possibility to alter the direction of the reaction by varying reaction conditions and using appropriate initiators permits one to perform directed synthesis of fluorinated compounds of various compositions.

Reactions of perfluoroalkyl iodides with organic substrates can be initiated in three different ways, *viz.*:

(1) by treating perfluoroalkyl iodides with reductants. The key steps in this process are the initial formation of the intermediate radical anion of perfluoroalkyl iodide and its dissociation into the perfluoroalkyl radical and the iodide anion;

(2) by treating perfluoroalkyl iodides with oxidants. As a result the reactant, possessing electrophilic properties, generates a radical cation. The latter reacts with perfluoroalkyl iodide to generate a radical anion $[\text{R}_\text{F}\text{I}]^{\cdot-}$, which is further decomposed to give a perfluoroalkyl radical;

(3) by treating perfluoroalkyl iodides with systems which generate alkyl or any other radicals themselves. The reaction of the latter with perfluoroalkyl iodide yields perfluoroalkyl radicals by-passing the formation of radical anions.

A vast body of experimental evidence on each of these approaches provides a guideline for new applications of perfluoroalkyl iodides. It seems therefore expedient to lay the main emphasis on these particular pathways of chemical transformations of perfluoroalkyl halides and sodium perfluoroalkanesulfonates.

1. Reactions of perfluoroalkyl iodides in the presence of reducing systems

The presence of an appropriate reductant is a main requirement for the activation of perfluoroalkyl halides and the intermediate formation of perfluoroalkyl radicals. Its specific function consists primarily in the generation of the corresponding radical anions from perfluoroalkyl halides.

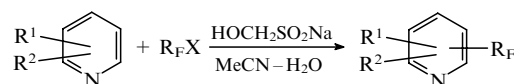
Various systems have been tested for this purpose, *viz.*, (1) formaldehyde–sodium sulfoxylate;¹⁹⁰ (2) sodium dithionite; (3) thiourea dioxide;^{170, 185} (4) metals and metal salts; (5) transition metal complexes. Each of these systems has characteristic features of its own; therefore, their effects must be considered in more detail.

a. The formaldehyde–sodium sulfoxylate system

The formaldehyde–sodium sulfoxylate system or rongalite ($\text{HOCH}_2\text{SO}_2\text{Na}$), is widely used in industry as a reductant. Its reaction with perfluoroalkyl iodides and bromides gives the corresponding salts of sulfinic acids. It was found that under special conditions this reagent can generate perfluoroalkyl radicals from both perfluoroalkyl iodides and perfluoroalkanesulfinic acid salts.

The reaction of perfluoroalkyl iodides and bromides with ethylene, ethylene derivatives and acetylene in polar solvents in the presence of compounds containing the SO_2^- anion (*e.g.*, $\text{Na}_2\text{S}_2\text{O}_4$, $\text{HOCH}_2\text{SO}_2\text{Na}$, *etc.*) (3 h, room temperature) yields addition products at the multiple bond in nearly quantitative yields.¹⁰¹

Rongalite was used for perfluoroalkylation of pyridine derivatives under the action of perfluoroalkyl iodides.^{191, 192, 196, 197}



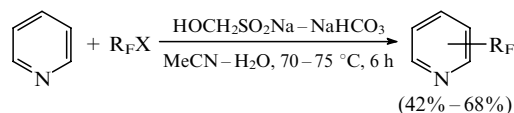
$\text{X} = \text{I}, \text{Br};$

$\text{R}^1 = \text{H}; \text{R}^2 = \text{H}, 3\text{-Me}, 4\text{-Me}, 4\text{-NH}_2; \text{R}^1 = 3\text{-Me}, \text{R}^2 = 5\text{-Me};$

$\text{R}^1 - \text{R}^2 = 2,3\text{-CH}=\text{CHCH}=\text{CH}$ (quinoline);

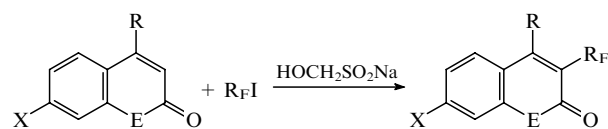
$\text{R}^1 - \text{R}^2 = 3,4\text{-CH}=\text{CHCH}=\text{CH}$ (isoquinoline).

It is worth noting that the reaction of the perfluoroalkyl iodides $\text{R}_\text{F}\text{I}$ with pyridine in the presence of the $\text{Na}_2\text{S}_2\text{O}_4-\text{NaHCO}_3$ system does not result in the formation of perfluoroalkylation products in acceptable yields, whereas an addition of $\text{HOCH}_2\text{SO}_2\text{Na}$ affords a mixture of α -, β - and γ -perfluoroalkylpyridines in sufficiently good yields.^{191, 192}

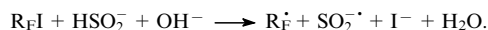


$\text{R}_\text{F}\text{X} = \text{C}_6\text{F}_{13}\text{I}, \text{C}_7\text{F}_{15}\text{I}, \text{C}_8\text{F}_{17}\text{I}, \text{ClC}_8\text{F}_{16}\text{I}, \text{C}_7\text{F}_{15}\text{Br}, \text{ClC}_6\text{F}_{12}\text{Br}.$

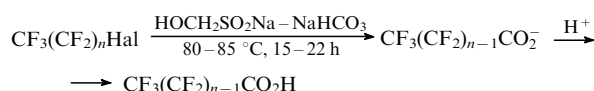
This reaction applied to coumarin gives 3-perfluoroalkylcoumarin; its S- and N-analogues can also be prepared in good yields.^{198, 199} However, in the case of the $\text{Na}_2\text{S}_2\text{O}_4$ –cetyltrimethylammonium bromide (CTMAB) system the yield of the target product is low.⁶²



$\text{E} = \text{O}$ (63%), S, NH; $\text{R}_\text{F} = \text{F}(\text{CF}_2)_6$; $\text{X} = \text{H}, \text{OH}.$

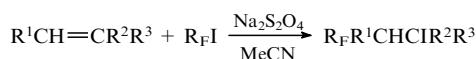
$$\text{Pyridine} + \text{Cl}(\text{CF}_2)_4\text{I} \xrightarrow[\text{MeCN-H}_2\text{O}, 60^\circ\text{C}, 5\text{ h}]{\text{HOCH}_2\text{SO}_2\text{Na}} \text{2-(CF}_2)_4\text{Clpyridine} \quad (68\%)$$
$$\text{HOCH}_2\text{SO}_5^- \longrightarrow \text{HSO}_5^- + \text{CH}_2\text{O}.$$


The reaction of polyfluoroalkyl iodides and -bromides containing 3 to 12 carbon atoms, viz., $\text{Cl}(\text{CF}_2)_n\text{I}$ ($n = 4, 6, 8$), $\text{CF}_3(\text{CF}_2)_n\text{I}$ ($n = 5-7$) and $\text{Cl}(\text{CF}_2)_n\text{NBr}$ ($n = 4, 6$), with the rongalite- NaHCO_3 system in bipolar aprotic solvents (MeCN, DMF) results in the formation of sodium polyfluorocarboxylates in high yields.^{185, 201-205} This approach is more convenient than the conventional method based on electrochemical fluorination of carboxylic acids and their derivatives.

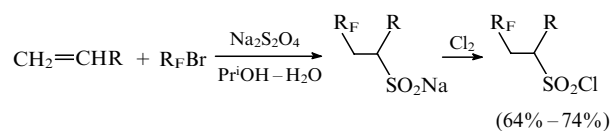


<i>n</i>	Hal	Yield (%)	<i>n</i>	Hal	Yield (%)
2	I	74	6	I	82
	Br	80		Br	70
3	I	82	7	I	70
	Br	—		Br	86
5	I	79	11	I	51
	Br	84		Br	—

Reactions of perfluoroalkyl iodides with ethylene and acetylene in polar solvents induced by sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) also permit the introduction of the perfluoroalkyl group into organic molecules. Thus the reaction of $\text{Cl}(\text{CF}_2)_6\text{I}$ with ethylene in the presence of the $\text{Na}_2\text{S}_2\text{O}_4\text{--NaHCO}_3$ system (3 h, room temperature) gives an addition product at the multiple bond, $\text{Cl}(\text{CF}_2)_6\text{CH}_2\text{CH}_2\text{I}$, in a nearly quantitative yield.^{186, 187, 211, 212} A similar reaction involves secondary perfluoroalkyl iodides, such as $\text{CF}_3\text{CFI}(\text{CF}_2)_4\text{SO}_2\text{F}$, $\text{CF}_3\text{CFI}(\text{CF}_2)_n\text{Cl}$ ($n = 2, 4$), $\text{CF}_3\text{CFI}(\text{CF}_2)_2\text{O}(\text{CF}_2)_2\text{SO}_3\text{Na}$ and $\text{CF}_3(\text{CF}_2)_2\text{OCFICF}_3$.^{213–215}

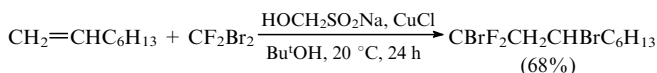
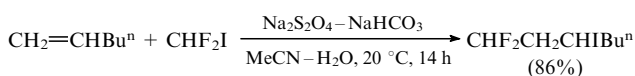
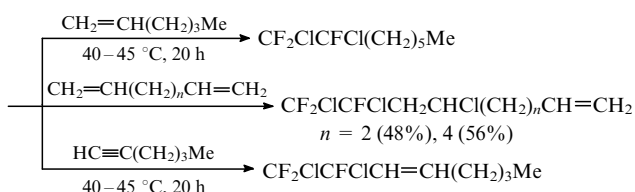


In the presence of sodium dithionite, perfluoroalkyl bromides react vigorously with alkenes in aqueous isopropyl alcohol at 60–70 °C to give addition products in good yields.²¹⁵

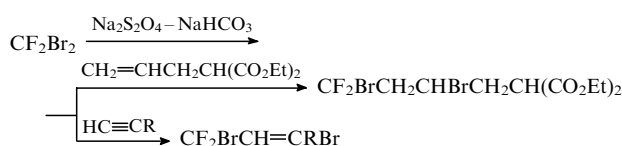


R = H, (CH₂)₃Me, (CH₂)₅Me, (CH₂)₇Me;
R_F = H(CF₂)₆, F(CF₂)₈, Cl(CF₂)₄, Cl(CF₂)₆.

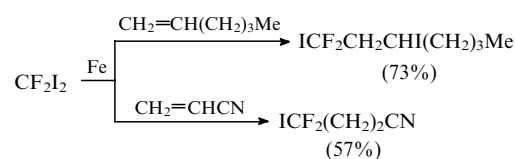
In the presence of sodium dithionite, rongalite or thiourea dioxide, CF_2Br_2 and CHF_2I react with terminal alkenes in aqueous acetonitrile or *tert*-butyl alcohol at room temperature or on cooling to give the corresponding adducts.^{196, 217, 218}


$$\text{CF}_2\text{ClCFCl}_2 \xrightarrow[\text{MeCN}-\text{H}_2\text{O}]{\text{Na}_2\text{S}_2\text{O}_4-\text{NaHCO}_3}$$


In the presence of sodium dithionite, CF_2Br_2 reacts with diethylallyl malonate, alkenes and alkynes; in the latter case, mixtures of *E*- and *Z*-isomers are formed in moderate yields (Table 6).^{196, 220}



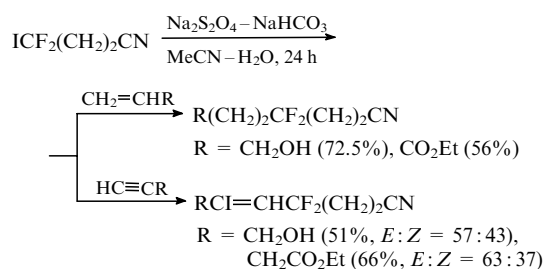
The reaction of difluorodiiodomethane with alkenes in the presence of iron at 40–50 °C gives compounds carrying the ICF₂ group.^{221, 222}



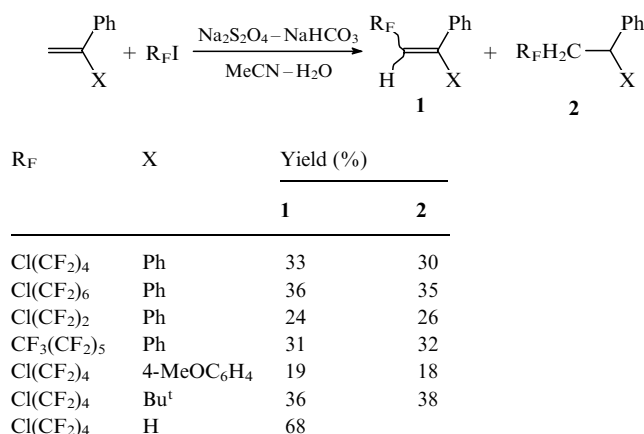
The latter also react with alkenes and alkynes in MeCN–H₂O in the presence of the Na₂S₂O₄–NaHCO₃ system at 30 °C, resulting in the formation of addition products at the multiple bond.²²²

Table 6. Reactions of alkenes and alkynes with CF₂Br₂ induced by reductants.

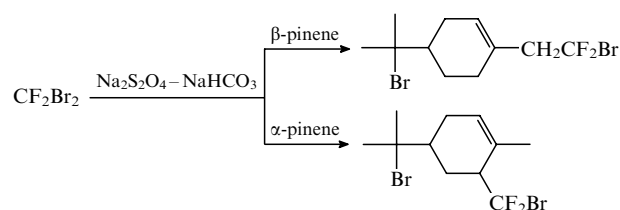
Substrate	Reductant	Yield (%)
Hex-1-ene	HOCH ₂ SO ₂ Na	85
	(NH ₂) ₂ C=SO ₂	80
	Na ₂ S ₂ O ₄	92
Oct-1-ene	HOCH ₂ SO ₂ Na	87
	Na ₂ S ₂ O ₄	88
Cyclohexene	HOCH ₂ SO ₂ Na	70
	(NH ₂) ₂ C=SO ₂	75
	Na ₂ S ₂ O ₄	75
Cyclooctene	Na ₂ S ₂ O ₄	80
Styrene	HOCH ₂ SO ₂ Na	50
Diallyl ether	Na ₂ S ₂ O ₄	85
α-Pinene	Na ₂ S ₂ O ₄	68
β-Pinene	Na ₂ S ₂ O ₄	75
Diethyl allylmalonate	Na ₂ S ₂ O ₄	80
Hex-1-yne	Na ₂ S ₂ O ₄	55
Hept-1-yne	Na ₂ S ₂ O ₄	53
Oct-1-yne	Na ₂ S ₂ O ₄	50
2,3-Dihydrofuran	Na ₂ S ₂ O ₄	78
3,4-Dihydro-2H-pyran	Na ₂ S ₂ O ₄	72
3,4-Dihydro-2H-pyran (excess)	Na ₂ S ₂ O ₄	76



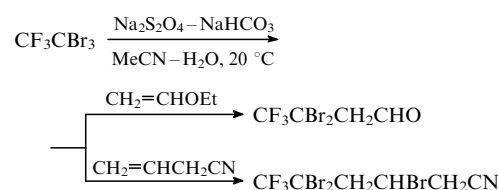
The reaction of Cl(CF₂)₄I with α-phenylstyrene in aqueous MeCN induced by the Na₂S₂O₄–NaHCO₃ system (4 h, 40 °C) gives the products **1** and **2** which contain no iodine atom.²²³



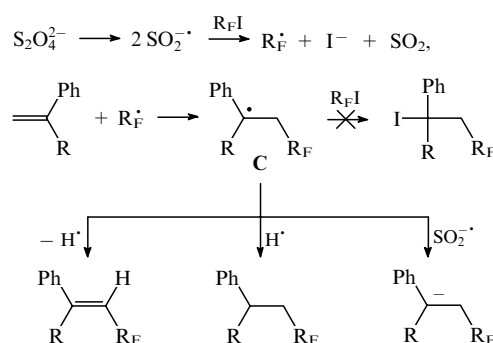
However, if styrene is used as a substrate, fluorine-containing oligomers are formed together with compound **1**.¹⁹⁶ Cyclohexene and cyclooctene manifest similar behaviour.¹⁹⁶ Under these conditions, CF₂Br₂ also reacts with α- and β-pinenes.^{196, 220}



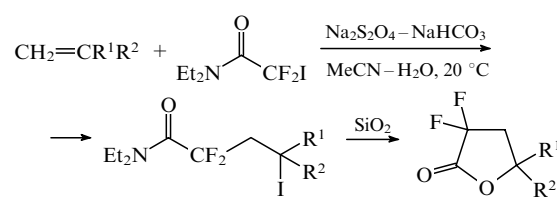
It was shown^{224–229} that the use of compounds containing different halogen atoms in the reaction of 1,1,1-tribromotrifluoroethane with alkenes yields addition products at the multiple bond.



The mechanism of generation of perfluoroalkyl radicals under the action of sodium dithionite and its subsequent reaction with alkenes is now well-established.¹⁵⁸ The transformations of the intermediate radical **C** were shown to occur in three different ways.



The reaction of perfluoroalkyl iodides with alkynes under sulfatodehalogenation conditions gives a mixture of *E*- and *Z*-adducts in very high yields.²³⁰ A similar reaction with alkenes was used in the synthesis of an α,α-difluoro-γ-lactone.²³¹



R¹ = R² = Alk, H.

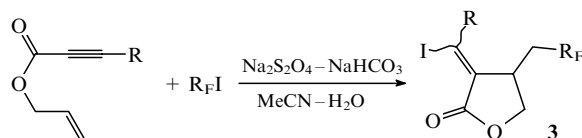
The reaction of CF₂=CFCF₂Cl with allyl alcohol in aqueous acetonitrile in the presence of the Na₂S₂O₄–NaHCO₃ system affords an adduct (1:1); treatment of the latter with zinc at 130–140 °C in ethylene glycol results in 1,1,2,3,3-pentafluoro-1,5-hexadiene,²³² which is further used in the synthesis of poly-fluorinated polymers.

In the presence of sodium dithionite, perfluoroalkyl iodides react also with allyl alcohol and unsaturated carboxylic acids to give addition products at the multiple bonds in high yields.²³³

A convenient and efficient procedure was developed for the direct introduction of the perfluoroalkyl group into unsaturated compounds which is based on the reaction of perfluoroalkyl iodides with alkene and alkyne derivatives induced by sulfur-containing systems. The main advantages of this method are its simplicity, high variability of functional groups, easy isolation of reaction products and regioselectivity. Moreover, these reagents

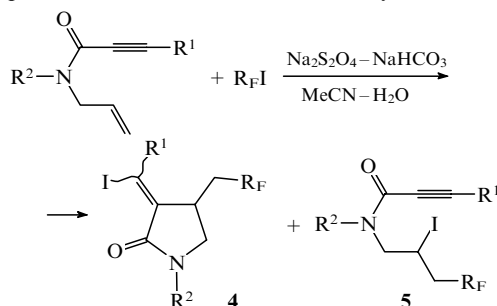
are neither toxic nor explosive, which makes them environmentally safe.

The presence of two multiple bonds in the substrate molecule favours the addition of R_F and I fragments to the alkene and the formation of a five-membered heterocycle of the type **3**. This reaction is regioselective.²⁰¹ Its strategy consists in the generation of a radical centre due to the cleavage of the F_2C-I bond, the addition of the radical formed at the double bond and subsequent cyclisation involving the radical centre and the multiple bond as a donor. Polyfluoroalkylated 3-iodoalkylidenetetrahydrofuran-2-one is formed as a result of generation of the perfluoroalkyl radical initiated by the reaction of R_F with $Na_2S_2O_4$ and subsequent formation of a five-membered heterocycle. This reaction occurs with high regioselectivity.²⁰¹



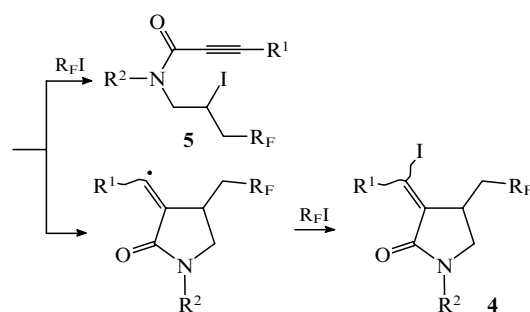
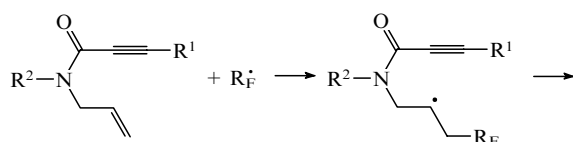
R	R_F	Yield (%)	<i>E</i> : <i>Z</i>
H	CF_3	44	32 : 68
H	$Cl(CF_2)_2$	47	60 : 40
H	$Cl(CF_2)_4$	50	52 : 48
Me	CF_3	80	95 : 5
Me	$Cl(CF_2)_2$	83	> 97 : 3
Me	$Cl(CF_2)_4$	82	> 97 : 3
$n-C_8H_{17}$	$Cl(CF_2)_2$	92	> 97 : 3

Similarly, perfluoroalkyl derivatives of 3-iodoalkylidene-2-pyrrolidone **4** and the acyclic amide **5** are formed in the perfluoroalkylation of *N*-allylprop-2-en- and *N*-allylbut-3-enamides by perfluoroalkyl iodides (or by polyfluoroalkyl iodides) in the presence of the $Na_2S_2O_4-NaHCO_3$ system.^{201, 211}



R^1	R^2	R_F	Yield (%)		<i>E</i> : <i>Z</i>
			4	5	
Me	Me	$Cl(CF_2)_2$	53	19	> 97 : 3
Me	Bn	$Cl(CF_2)_2$	50	35	> 97 : 3
Me	Bn	$Cl(CF_2)_4$	49	29	> 97 : 3
Pr^n	Bn	$Cl(CF_2)_2$	41	23	> 97 : 3
Pr^n	Bn	$Cl(CF_2)_4$	43	27	> 97 : 3
H	MeCO	$Cl(CF_2)_2$	46	0	52 : 48
Me	PhCO	$Cl(CF_2)_2$	70	0	> 97 : 3
Me	PhCO	$Cl(CF_2)_4$	60	0	> 97 : 3
Me	OTs	CF_3	72	0	> 97 : 3
Me	OTs	$Cl(CF_2)_4$	83	0	> 97 : 3

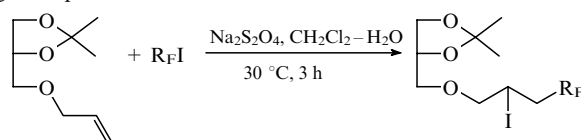
Presumably, this reaction occurs by the following scheme:



Cyclisation induced by the intermediate radical is successfully used for the construction of cyclic systems.²³⁴

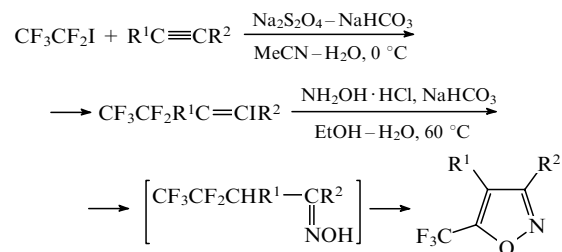
It is worth noting that in reactions with alkynes perfluoroalkyl iodides form mixtures of *E*- and *Z*-adducts in the presence of sodium dithionite, whereas perfluoroalkyl bromides and trichloro-1,1,1-trifluoroethane yield exclusively sulfonates.²³⁰

Generally, if the starting compound contains a double bond, its treatment with perfluoroalkyl iodides in the presence of the $Na_2S_2O_4-NaHCO_3$ system results in the formation of addition products as is the case in the reaction of perfluoroalkyl iodides with *O*-allyl-*O*-isopropylidenglycerol and crown ethers containing multiple bonds in a $CH_2Cl_2-H_2O$ mixture.^{235, 236}



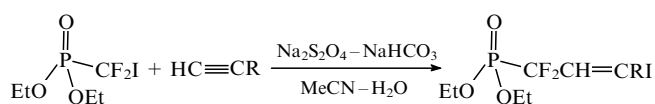
$R_F = F(CF_2)_8$ (72%), $F(CF_2)_6$ (59%), $Cl(CF_2)_6$ (55%), $Cl(CF_2)_8$ (68%).

The addition products of perfluoroalkyl iodides at the triple bond can be used in the synthesis of heterocyclic compounds, e.g., 5-perfluoroalkyl-substituted isoxazoles.^{237, 238}

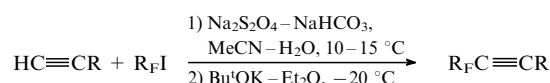


$R^1 = H$, $R^2 = CH_2OH$.

Diethyl difluoroiodomethylphosphonate was also introduced in the reaction with alkynes²²² to give a mixture of isomers the ratio of which depends on the nature of the substituent at the triple bond (Table 7).



Perfluoroalkyl derivatives of alkynes are formed in the reaction of alkynes with perfluoroalkyl iodides and subsequent treatment with a base as a result of elimination of HI from the adducts formed.²³⁵⁻²⁴⁰



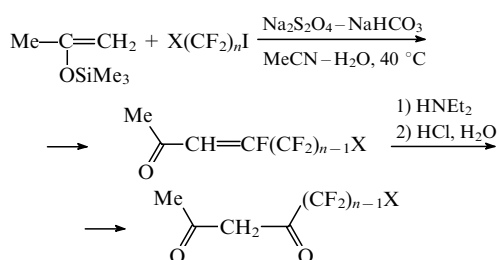
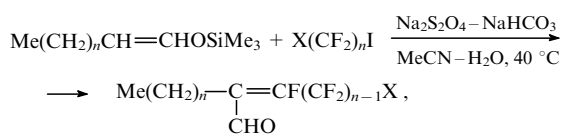
R_F	R	Yield (%)	R_F	R	Yield (%)
$Cl(CF_2)_2$	$n-C_6H_{13}$	47	$Cl(CF_2)_4$	$n-C_8H_{17}$	73
$Cl(CF_2)_2$	$n-C_8H_{17}$	74	$Cl(CF_2)_4$	$(CH_2)_6OH$	76
$Cl(CF_2)_2$	$(CH_2)_9OH$	82	$Cl(CF_2)_8$	Pr^n	78
$Cl(CF_2)_4$	Pr^n	52			

Table 7. The reaction of diethyl difluoroiodomethylphosphonate with alkynes $\text{HC}\equiv\text{CR}$ in the presence of the $\text{Na}_2\text{S}_2\text{O}_4\text{--NaHCO}_3$ system in $\text{MeCN--H}_2\text{O}$.²²²

R	<i>t</i> /h	Yield (%)	<i>E</i> : <i>Z</i>
(CH_2) ₃ Me	3	79	82:18
	0.17	41	52:48
CH_2OH	3	74	50:50
CO_2Me	4	65	100:0
CO_2Et	4	67	100:0
	0.17	26	100:0
CH_2OMe	3	75	57:43
Ph	3	62	72:28
CH_2OEt	3	72	59:41
CONMe_2	4	56	100:0

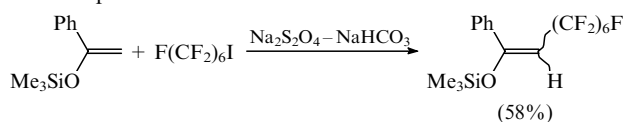
Note. The $\text{ICF}_2\text{P}(\text{O})(\text{OEt})_2\text{:HC}\equiv\text{CR}:\text{Na}_2\text{S}_2\text{O}_4:\text{NaHCO}_3$ ratio is 1:2:1:1.

The reaction of silylenol ethers with perfluoroalkyl iodides in the presence of the $\text{Na}_2\text{S}_2\text{O}_4\text{--NaHCO}_3$ system results in the formation of perfluoroalkylated α,β -unsaturated aldehydes and ketones.^{241–245} Heating of the latter with HNEt_2 (or piperidine) and acid hydrolysis give the corresponding β -dicarbonyl compounds.

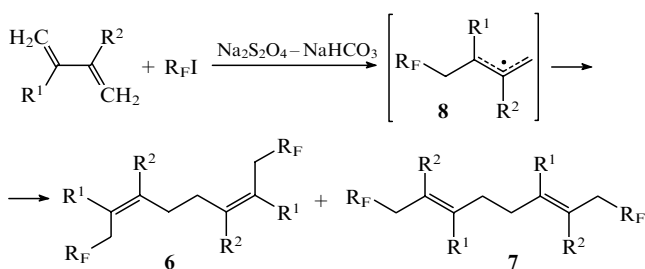


$\text{X} = \text{Cl}; n = 4, 6, 8; \text{X} = \text{F}; n = 6, 8.$

Trimethylsilyl ethers of the enol forms of acetophenone and methyl vinyl ketone react with perfluoroalkyl iodides in the presence of the $\text{Na}_2\text{S}_2\text{O}_4\text{--NaHCO}_3$ system to give hydrogen substitution products at the double bond.²⁴²

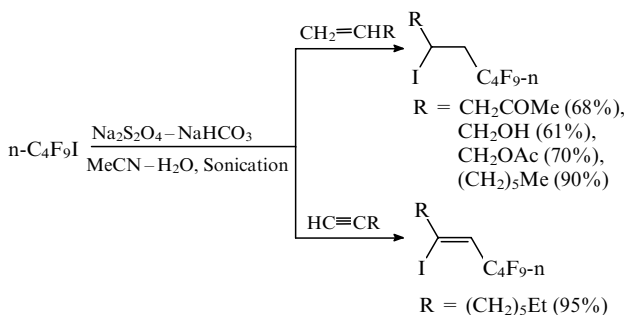


It should be noted that the intermediate radical is capable of dimerisation; thus the dimeric products **6** and **7** are formed from butadiene derivatives in reactions involving allylic radicals **8**.²⁴⁶

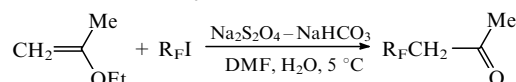
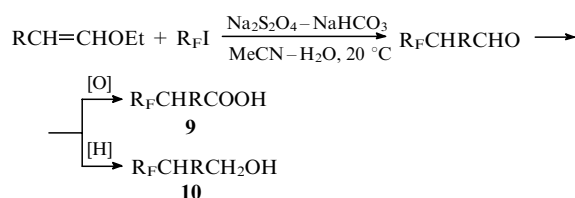


$\text{R}_\text{F} = \text{Cl}(\text{CF}_2)_n (n = 2, 4), \text{CF}_3(\text{CF}_2)_3; \text{R}^1 = \text{R}^2 = \text{H}, \text{Me}.$

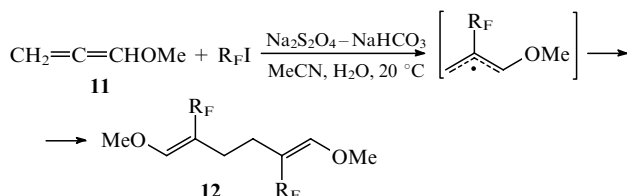
The rates of reactions of perfluoroalkyl halides with alkenes and alkynes can be increased by sonication.^{206, 235}



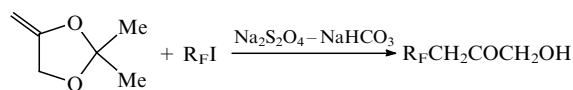
α -Perfluoroalkyl derivatives of aldehydes formed as intermediate products in the synthesis of valuable fluorine-containing blocks²²⁶ are further used in the synthesis of heterocyclic compounds.^{227, 240} Polyfluorinated aldehydes or ketones are formed in reactions of vinyl ethers with perfluoroalkyl iodides and are further transformed into either the corresponding acids **9** or alcohols **10**.²⁴⁷



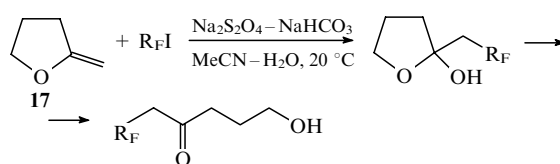
Compound **11** containing the allene group, like dienes, form an intermediate radical in the reaction with perfluoroalkyl iodides; its dimerisation yields the diether **12**.²³⁶



Perfluoroalkyl iodides $\text{n-C}_6\text{F}_{13}\text{I}$ and $\text{Cl}(\text{CF}_2)_n\text{I}$ ($n = 2, 4, 6, 8$) react with 4-methylenedioxolane in the presence of the $\text{Na}_2\text{S}_2\text{O}_4\text{--NaHCO}_3$ system resulting in ring opening.²⁴⁸



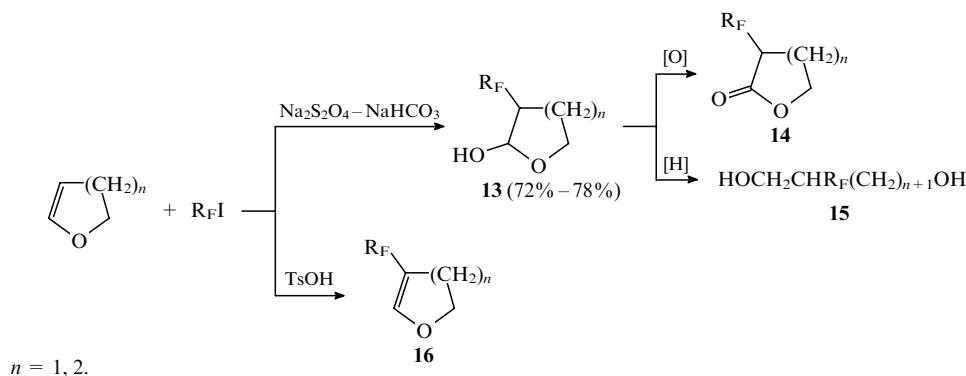
Cyclic ethers (2,3-dihydrofuran and 3,4-dihydro-2*H*-pyran) react with $\text{R}_\text{F}\text{I}$ [$\text{R}_\text{F} = \text{Cl}(\text{CF}_2)_n$, where $n = 4, 6, 8$; $\text{F}(\text{CF}_2)_n$, where $n = 6, 8$]²²⁶ or with CF_2Br_2 ^{196, 225} in the presence of the $\text{Na}_2\text{S}_2\text{O}_4\text{--NaHCO}_3$ system to produce 2-polyfluoroalkylhemiacetals **13** which can be oxidised to the corresponding lactones **14** or reduced to the diols **15**.^{226, 249} On the other hand, the hydrogen substitution product at the multiple bond **16** is formed in the presence of *p*-toluenesulfonic acid (Scheme 1).



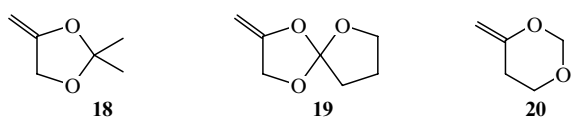
$\text{R}_\text{F} = \text{n-C}_6\text{F}_{13}, \text{Cl}(\text{CF}_2)_n (n = 2, 4, 6, 8).$

Perfluoroalkyl iodides react with heterocyclic compounds **17–20** containing an α -methylene substituent in the presence of

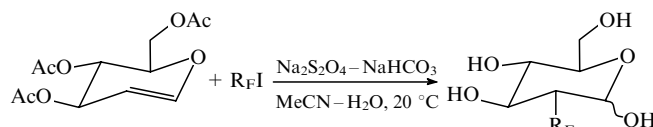
Scheme 1



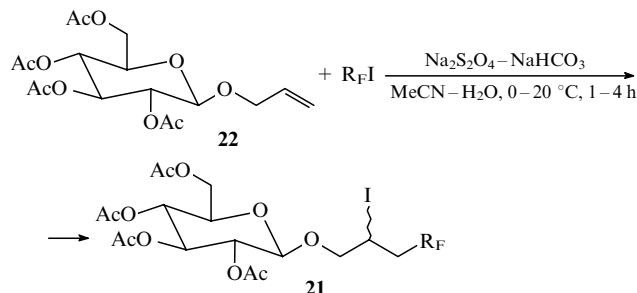
the $\text{Na}_2\text{S}_2\text{O}_4 - \text{NaHCO}_3$ system with the formation of ring-opening products.²⁵⁰



Carbohydrates containing perfluoroalkyl substituents, *e.g.*, 2- R_F -2-deoxy-D-glucose, are prepared by perfluoroalkylation of glycals by perfluoroalkyl iodides induced by the $\text{Na}_2\text{S}_2\text{O}_4 - \text{NaHCO}_3$ system.^{197, 207, 251 - 258}

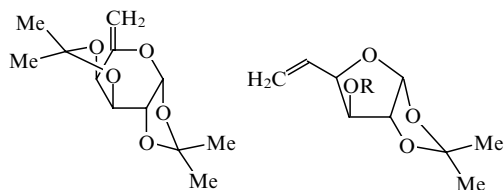


Perfluoroalkyl-substituted carbohydrates, *e.g.*, 2-iodo-3-perfluoroalkylpropyl-2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranoside (**21**), can be synthesised by perfluoroalkylation of allyl glucopyranoside **22**. These compounds were found to be useful intermediates and can be used as surfactants and emulsifiers.^{250, 259 - 266}



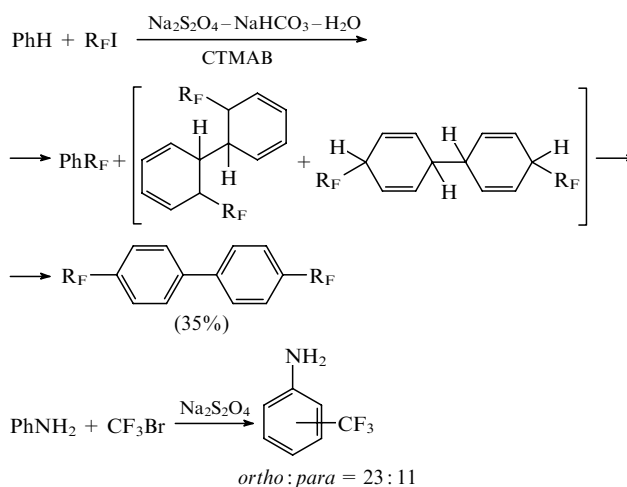
$\text{R}_\text{F} = \text{C}_4\text{F}_9$ (86%), C_6F_{13} (83%), C_8F_{17} (78%), $\text{C}_{10}\text{F}_{21}$ (71%).

Perfluoroalkyl iodides add at the multiple bond of hex-5-enopyranose and -furanose ($\text{R} = \text{CH}_2\text{Ph}$, Me) in the presence of $\text{Na}_2\text{S}_2\text{O}_4$.²⁶²



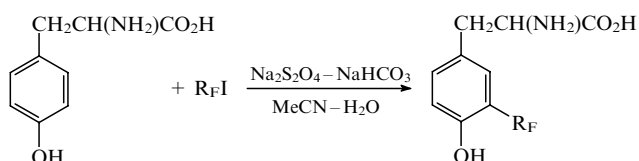
Under ordinary conditions, benzene does not react with perfluoroalkyl iodides; however, under conditions of phase-transfer catalysis with CTMAB it yields perfluoroalkylation products and dimerisation products of intermediate cationic σ -complexes.^{212, 267 - 269} Perfluoroalkylation of aromatic compounds containing amino or hydroxy substituents with bromotrifluoro-

methane or long-chain perfluoroalkyl iodides occurs at the *ortho*- and *para*-positions.^{212, 267 - 269}

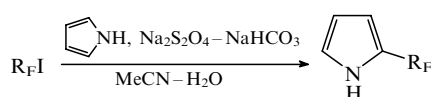


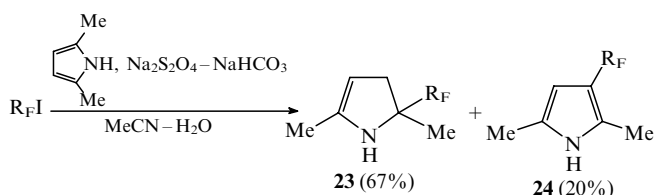
Ortho- and *para*-perfluoroalkylphenols can easily be prepared from phenol²⁷⁰ and its *para*-substituted derivatives^{252, 271} in the presence of an alkali. For example, in the presence of NaOH *p*-cresol reacts with $\text{Cl}(\text{CF}_2)_6\text{I}$ in DMF containing $\text{Na}_2\text{S}_2\text{O}_4 - \text{NaHCO}_3$ to give 2- ω -chloroperfluorohexyl-*p*-cresol in 60% yield.²⁷⁰ 2,6-Diperfluoroalkyl derivatives can also be formed.²⁷¹

The $\text{Na}_2\text{S}_2\text{O}_4 - \text{NaHCO}_3$ system was efficient in the perfluoroalkylation of biologically active compounds containing a phenolic fragment. A procedure was developed for introducing perfluoroalkyl substituents into the aromatic ring of tyrosine.²⁷²

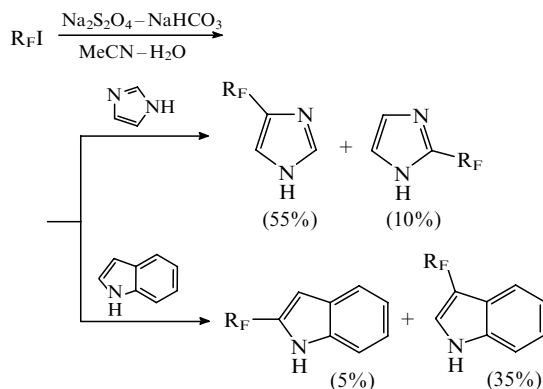


α -Perfluoroalkyl-substituted derivatives are formed in high yields upon treatment of pyrrole with perfluoroalkyl iodides in the presence of the $\text{Na}_2\text{S}_2\text{O}_4 - \text{NaHCO}_3$ system.²⁷³ However, high hydrolytic lability of the fluorine atoms of the α - CF_2 group should be kept in mind. It is of note that 2,5-dimethylpyrrole yields both addition (**23**) and substitution products of the hydrogen atom of the pyrrole ring (**24**).^{274 - 277}



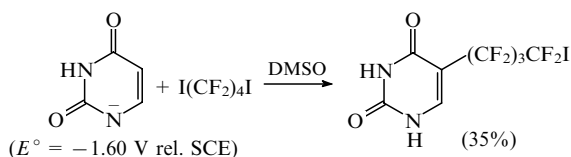
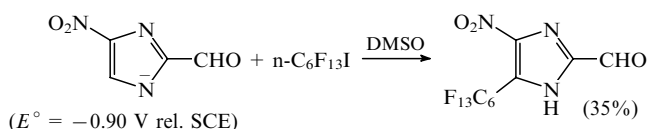


Perfluoroalkylation of other nitrogen-containing heterocyclic compounds is also possible.²⁷³

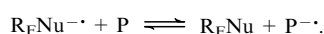
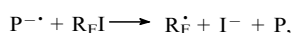
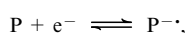


Perfluoroalkyl sulfones are synthesised in the reaction of alkenes $\text{H}_2\text{C}=\text{CHR}$ ($\text{R} = \text{CN}, \text{MeCO}$) with sodium perfluoroalkanesulfonates $\text{R}_\text{F}\text{SO}_2\text{Na}$ ($\text{R}_\text{F} = \text{C}_4\text{F}_9, \text{ClC}_4\text{F}_8$) obtained by treatment of perfluoroalkyl iodides with sodium dithionite.¹⁸⁸

It may thus be concluded that perfluoroalkyl radicals can be formed from perfluoroalkyl halides under the action of other radical anions capable of generating radical anions of perfluoroalkyl halides. Indeed, Medebielle *et al.*²³⁹ who studied the reduction of CF_3Br , $n\text{-C}_4\text{F}_9\text{I}$, $n\text{-C}_6\text{F}_{13}\text{I}$ and $\text{I}(\text{CF}_2)_4\text{I}$ using terephthalonitrile, nitrobenzene and 4-nitropyridine *N*-oxide as messengers ($E^\circ = -1.60, -1.10$ and -0.79 V rel. SCE, respectively) demonstrated the efficiency of perfluoroalkylation of *N*-anions of the heterocyclic series (*e.g.*, imidazole, adenine, xanthine, uracil, cytosine, barbituric acid, lumazine, theophylline) by intermediate perfluoroalkyl radicals.



This reaction occurs in accordance with the following scheme. The initial electrochemically generated 4-nitropyridine *N*-oxide (P) radical anion induces the reduction of perfluoroalkyl halide to the corresponding radical anion which is further transformed into the perfluoroalkyl radical. The latter reacts with the *N*-anion to yield a new radical anion which ultimately yields the final product and the radical anion of the 'messenger', *viz.*,



In the case of perfluoroalkyl halides, the reaction mechanism represents a modified version of the classical $\text{S}_{\text{RN}}1$ mechanism where the electron transfer occurs without the intermediate formation of the substrate radical anion. The perfluoroalkyl

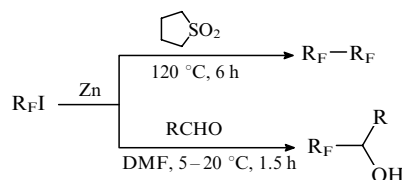
radical thus generated attacks the carbon atom of the *N*-anion of the heterocyclic compound, eventually resulting in the formation of the reaction product.

This methodology describes the perfluoroalkylation of organic substrates by perfluoroalkyl halides as a reduction in the presence of catalysts of the 4-nitropyridine *N*-oxide type.

c. Reactions of perfluoroalkyl iodides and -bromides catalysed by transition metals and their derivatives

Catalytic effects of metals and their salts. Various initiators of addition reactions of perfluoroalkyl iodides and -bromides to the multiple bonds $\text{C}=\text{C}$ are presently known. An important role in the generation of perfluoroalkyl radicals is played by transition metal derivatives (mostly, zero-valent compounds)^{278, 279} and their complexes^{180, 280–283} used as both reagents and catalysts of diverse reactions.^{180, 278, 282, 283} Reactions of perfluoroalkyl iodides with alkenes and alkynes are especially efficient in the presence of Ru, Ni, W, Mo,^{180, 282, 283} Sn,^{284, 285} Fe,^{286, 287} Mg,^{288, 289} Cu,^{290–294} Raney Ni (RaNi),^{295–297} Pt,^{298, 299} Mn^{II}, Hg^I,³⁰⁰ Ru^{II},³⁰¹ Rh,³⁰² Me₃Al,²¹⁷ Et₃B,^{303–308} Zn,^{197, 309} and Pd⁰ (see Refs 197, 278, 310) and result in the formation of addition products at the multiple bond.^{278, 279} Reactions of perfluoroalkyl iodides with benzene in the presence of metals (Rh, Pd, Pt, Ru, Cu, RaNi, Co) and aqueous potassium hydrogencarbonate give perfluoroalkylbenzenes.^{311, 312} It is noteworthy that disubstitution occurs with low yields.

The role of metals consists in reductive generation of the radical $\text{R}_\text{F}^\cdot$ from $\text{R}_\text{F}\text{I}$. Further transformations depend on the type of the substrate and may occur either as subsequent addition of the radical $\text{R}_\text{F}^\cdot$ at the multiple bond ($\text{C}=\text{C}$) or as substitution of a halogen or hydrogen atom at the carbon atom of the multiple bond. Thus perfluoroalkyl iodides give perfluoroalkanes in the presence of zinc in sulfolane or in H_2O ;³¹³ in DMF they react with aldehydes to give the corresponding alcohols.³¹⁴



The reaction of bromotrifluoromethane with aldehydes and zinc in *N*-methylpyrrolidone yields alcohols;³¹⁵ trifluoroacetaldehyde is formed from DMF under conditions of cathode synthesis.³¹⁶

It should be noted that reactions of perfluoroalkyl iodides and -bromides with electrophiles can also be catalysed by other metals. Thus the reaction of bromotrifluoromethane with chlorotrimethylsilane in the presence of aluminium powder in *N*-methylpyrrolidone yields trimethyl(trifluoromethyl)silane (yield 62%).³¹⁷ In the presence of cadmium, perfluoroalkanes are formed in 72% to 90% yield.³¹⁸ The reaction of $\text{Cl}(\text{CF}_2)_4\text{I}$ with $\text{Bu}^n\text{CH}=\text{CH}_2$ in the presence of Mg results in the addition product $\text{Bu}^n\text{CHICH}_2(\text{CF}_2)_4\text{Cl}$ in high yield, the reaction with $\text{Bu}^n\text{C}\equiv\text{CH}$ yields a mixture of (*E*)- and (*Z*)- $\text{Cl}(\text{CF}_2)_4\text{CH}=\text{CIBu}^n$ (Ref. 288).

Various reactions of perfluoroalkyl iodides with aromatic compounds (Table 8) and alkenes in the presence of copper have been described.^{319–322} In these reactions, diethylene glycol, acetonitrile and acetic anhydride are used as solvents.

The reaction of perfluoroalkyl iodides with cyclohexene in the presence of catalytic amounts of copper gives addition products at the multiple bond and reduction products.

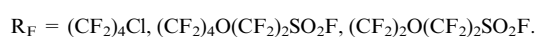
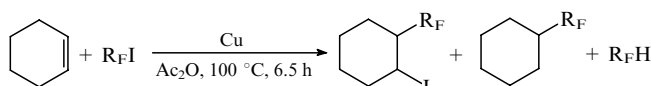
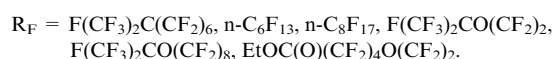
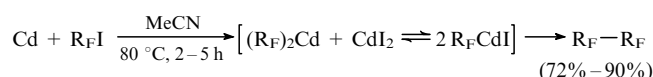


Table 8. Reactions of bromo- and iodoaromatic compounds with perfluoroalkyl iodides R_FI in the presence of copper.³²¹

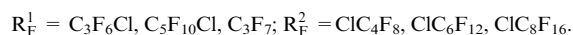
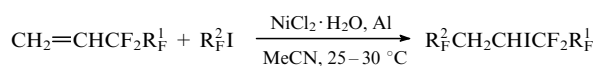
ArHal	R_F	Reaction conditions			Product	Yield (%)
		solvent	$T/^\circ\text{C}$	t/h		
PhI	n-C ₇ F ₁₅	DMSO	125	23	n-C ₇ F ₁₅ Ph	78
	n-C ₈ F ₁₇	DMSO	130	15	n-C ₈ F ₁₇ Ph	83
C ₁₀ H ₇ Br	n-C ₇ F ₁₅	DMSO	125	34	n-C ₇ F ₁₅ C ₁₀ H ₇	45
C ₁₀ H ₇ I	n-C ₇ F ₁₅	DMSO	125	48	n-C ₇ F ₁₅ C ₁₀ H ₇	89
	n-C ₈ F ₁₇	C ₅ H ₅ N	120	16	n-C ₈ F ₁₇ C ₁₀ H ₇	96

The reactions catalysed by metals (*e.g.*, Zn, Cd) seem to occur via the intermediate formation of organometallic compounds, *viz.*, an organozinc compound of the $\text{CF}_3\text{ZnBr} \cdot L_n$ type (see Ref. 314) or an organocadmium compound,³¹⁸ which further generate perfluoroalkyl radicals.



Hence the initiation of the cleavage of the C–Hal bond under the action of metals is one of the simplest and convenient methods for the activation of reactions of R_FI with alkenes and alkynes.²⁸⁸

It would be natural to expect that a similar effect will be produced by a combination of transition metal salts and zero-valent metals. Indeed, the $\text{NiCl}_2 \cdot 6\text{H}_2\text{O} - \text{Al}$ system efficiently initiates the reactions of R_FI with $R_F\text{CH}=\text{CH}_2$ resulting in the formation of addition products at the multiple bond, albeit, in moderate yields.³²³ For example, the yields of the adducts formed in the reaction of alkenes with R_FI in MeCN in the presence of 20 mol. % of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 2 equiv. Al (25–30 °C, 12 h) (Table 9) were 45%–60%.³²³ Zinc can replace aluminium in this reaction.³²⁴



An interesting transformation occurred when perfluoroalkyl iodides, -bromides and -chlorides were heated in DMF in the presence of aluminium-promoted Sn^{II} ($\text{SnCl}_2 - \text{Al}$)³²⁵ or Pb^{II} ($\text{PbBr}_2 - \text{Al}$).^{326–329} This reaction resulted in the formation of perfluoroalkylaldehyde monohydrates.^{325–329}



Reagents and conditions	R_FX	Yield (%)	Reagents and conditions	R_FX	Yield (%)
(a) SnCl_2 , Al,	$\text{Cl}(\text{CF}_2)_4\text{I}$	80	(b) PbCl_2 , Al	$\text{H}(\text{CF}_2)_4\text{Cl}$	80
20 °C,	$\text{Cl}(\text{CF}_2)_6\text{I}$	97		$\text{H}(\text{CF}_2)_6\text{Cl}$	85
10 h	$\text{Cl}(\text{CF}_2)_8\text{I}$	88		$\text{H}(\text{CF}_2)_8\text{Cl}$	88
	$\text{C}_4\text{F}_9\text{I}$	90		$\text{CH}_2=\text{CH}(\text{CF}_2)_4\text{Cl}$	82
	$\text{C}_6\text{F}_{13}\text{Br}$	84		$\text{CH}_2=\text{CH}(\text{CF}_2)_6\text{Cl}$	86
	$\text{C}_8\text{F}_{17}\text{Br}$	89		$\text{Bu}^n\text{CHICH}_2(\text{CF}_2)_4\text{Cl}$	91
				$\text{Bu}^n\text{CHICH}_2(\text{CF}_2)_6\text{Cl}$	93

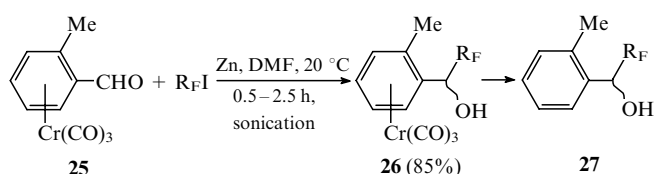
The yields of reaction products and reaction conditions are listed in Tables 10 and 11.

The perfluoroalkylation of DMF by perfluoroalkyl iodides and α,ω -dibromoperfluoroalkanes in the presence of $\text{Al}-\text{SnCl}_2$ or $\text{Al}-\text{PbBr}_2$ is strongly accelerated by sonication³³⁰ which has recently found wide application in the activation of organic reactions.^{331–333} Thus the reaction occurring under normal conditions usually lasts from 4 to 24 h, whereas that subjected to sonication is completed within 0.25–3 h. The possibility of performing perfluoroalkylation with perfluoroalkyl iodides in

the presence of metals (*e.g.*, zinc, magnesium, *etc.*) using sonication has been demonstrated.^{255, 334–337}

The reaction of cyclohexanone with $\text{C}_4\text{F}_9\text{I}$ in hexane catalysed by magnesium and activated by sonication results in 1-perfluorobutylcyclohexanol (yield ~ 81%).³³⁶

Perfluoroalkylation occurs in the presence of zinc in THF and is catalysed by the triphenylphosphine–palladium complex. In the absence of catalysts, the reactions of perfluoroalkyl iodides with compounds containing a carbonyl group are carried out using zinc in DMF. For example, the reaction of perfluoroalkyl iodides with the *o*-tolualdehyde–chromium tricarbonyl **25** complex yields the corresponding alcohols **26** which eliminate $\text{Cr}(\text{CO})_3$ to give the alcohols **27**.³³⁸

**Table 9.** Reactions of fluorine-containing alkenes $\text{CH}_2=\text{CHCF}_2\text{R}_F^1$ with perfluoroalkyl iodides R_F^2I (25–30 °C, 12 h, molar ratio $\text{R}_2\text{F}_2\text{I} : \text{NiCl}_2 \cdot 6\text{H}_2\text{O} = 2.0 : 1.0 : 0.2$ or $5.0 : 1.0 : 0.2$).³²³

R_F^1	R_F^2	Product	Yield (%)
$\text{C}_3\text{F}_6\text{Cl}$	ClC_4F_8	$\text{ClC}_4\text{F}_8\text{CH}_2\text{CH}=\text{CFC}_3\text{F}_6\text{Cl}$	55
	$\text{ClC}_6\text{F}_{12}$	$\text{ClC}_6\text{F}_{12}\text{CH}_2\text{CH}=\text{CFC}_3\text{F}_6\text{Cl}$	56
	$\text{ClC}_8\text{F}_{16}$	$\text{ClC}_8\text{F}_{16}\text{CH}_2\text{CH}=\text{CFC}_3\text{F}_6\text{Cl}$	55
$\text{C}_5\text{F}_{10}\text{Cl}$	ClC_4F_8	$\text{ClC}_4\text{F}_8\text{CH}_2\text{CH}=\text{CFC}_5\text{F}_{10}\text{Cl}$	58
	$\text{ClC}_6\text{F}_{12}$	$\text{ClC}_6\text{F}_{12}\text{CH}_2\text{CH}=\text{CFC}_5\text{F}_{10}\text{Cl}$	60
	$\text{ClC}_8\text{F}_{16}$	$\text{ClC}_8\text{F}_{16}\text{CH}_2\text{CH}=\text{CFC}_5\text{F}_{10}\text{Cl}$	59
C_3F_7	$\text{ClC}_6\text{F}_{12}$	$\text{ClC}_6\text{F}_{12}\text{CH}_2\text{CH}=\text{CFC}_3\text{F}_7$	45
	$\text{ClC}_8\text{F}_{16}$	$\text{ClC}_8\text{F}_{16}\text{CH}_2\text{CH}=\text{CFC}_3\text{F}_7$	50

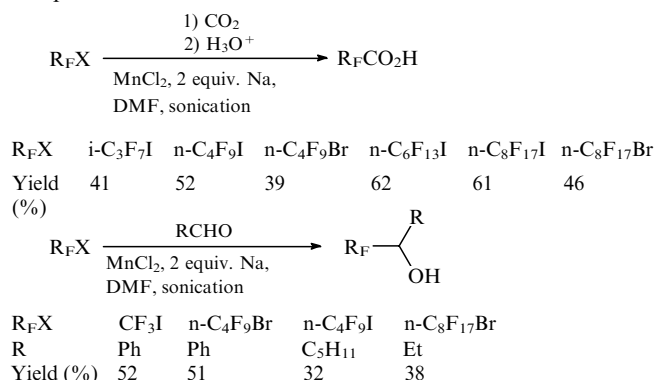
Table 10. The reaction of perfluoroalkyl iodides with DMF in the presence of the $\text{SnE}_2 - \text{Al}$ system.³²⁵

R_FX	SnE_2	Reaction conditions		Product	Yield (%)
		$T/^\circ\text{C}$	t/h		
$\text{Cl}(\text{CF}_2)_4\text{I}$	SnCl_2	16	6	$\text{Cl}(\text{CF}_2)_4\text{CHO}$	80
	SnCl_2	15	10	$\text{Cl}(\text{CF}_2)_4\text{CHO}$	88
	SnBr_2	15	6	$\text{Cl}(\text{CF}_2)_4\text{CHO}$	83
$\text{Cl}(\text{CF}_2)_6\text{I}$	SnCl_2	15	8	$\text{Cl}(\text{CF}_2)_6\text{CHO}$	97
	SnBr_2	15	9	$\text{Cl}(\text{CF}_2)_6\text{CHO}$	75
	SnF_2	15	5	$\text{Cl}(\text{CF}_2)_6\text{CHO}$	85
$\text{Cl}(\text{CF}_2)_8\text{I}$	SnBr_2	15	10	$\text{Cl}(\text{CF}_2)_8\text{CHO}$	79
	SnCl_2	15	8	$\text{F}(\text{CF}_2)_4\text{CHO}$	90
	SnCl_2	15	12	$\text{F}(\text{CF}_2)_6\text{CHO}$	84
$\text{F}(\text{CF}_2)_8\text{Br}$	SnCl_2	15	12	$\text{F}(\text{CF}_2)_8\text{CHO}$	89
	SnBr_2	15	15	$\text{F}(\text{CF}_2)_8\text{CHO}$	74
	SnF_2	15	6	$\text{F}(\text{CF}_2)_8\text{CHO}$	90

Table 11. The synthesis of polyfluorinated aldehydes and their monohydrates from perfluoroalkyl halides and DMF in the presence of aluminium-activated salts with and without sonication.³³⁰

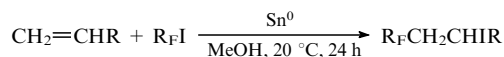
R _F X	Sonication	Time /h	Product	Yield (%)
Catalyst — SnCl ₂				
C ₄ F ₉ I	+	0.25	C ₄ F ₉ CHO	41
C ₆ F ₁₃ I	—	24	C ₆ F ₁₃ CH(OH) ₂ , C ₆ F ₁₃ CHO	80, 65
	+	0.25	C ₆ F ₁₃ CH(OH) ₂ , C ₈ F ₁₇ CHO	60, 65
C ₈ F ₁₇ I ₂	+	0.25	C ₈ F ₁₇ CH(OH) ₂ , C ₈ F ₁₇ CHO	78, 65
BrC ₈ F ₁₆ Br	+	3	(HO) ₂ CHC ₈ F ₁₆ CH(OH) ₂ , OHC ₈ F ₁₆ CHO	90, 69
Catalyst — PbBr ₂				
C ₄ F ₉ I	+	0.25	C ₄ F ₉ CHO	50
C ₆ F ₁₃ I	—	16	C ₆ F ₁₃ CH(OH) ₂ , C ₆ F ₁₃ CHO	74, 65
	+	0.25	C ₆ F ₁₃ CH(OH) ₂ , C ₆ F ₁₃ CHO	70, 62
C ₈ F ₁₇ I	+	0.25	C ₈ F ₁₇ CH(OH) ₂ , C ₈ F ₁₇ CHO	70, 60
BrC ₆ F ₁₂ Br	—	4	(HO) ₂ CHC ₆ F ₁₂ CH(OH) ₂ , OHC ₆ F ₁₂ CHO	80, 65
	+	1.5	(HO) ₂ CHC ₆ F ₁₂ CH(OH) ₂ , OHC ₆ F ₁₂ CHO	87, 60
BrC ₈ F ₁₆ Br	+	1.5	(HO) ₂ CHC ₈ F ₁₆ CH(OH) ₂ , OHC ₈ F ₁₆ CHO	83, 60

More recent studies³³⁸ demonstrated that sonication can be used in reactions of perfluoroalkyl iodides and -bromides with various carbonyl compounds and alkyl halides in the presence of MnCl₂—Na and AgBr—Li systems.³³⁹ This finding has led to the development of a simple procedure for the synthesis of perfluoro-carboxylic acids and partially fluorinated secondary alcohols using carbon dioxide and aldehydes, respectively. In this case, sodium and lithium are used as reductants for the formation of active metals (manganese and silver), which yield reactive organometallic derivatives with perfluoroalkyl halides. The organometallic derivatives enter into the reaction with the carbonyl compound.



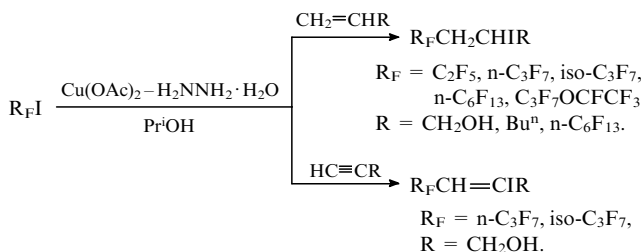
The activity of perfluoroalkyl halides decreases in the following order: R_FI > R_FBr ≫ R_FCl.

The Sn—AgOAc and Sn—Cu₂Cl₂ systems effectively catalyse reactions of perfluoroalkyl iodides with alkenes under relatively mild conditions.²⁸⁴ Methanol is the most suitable solvent for these reactions. Joint use of metallic Sn and Al produces the same effect.



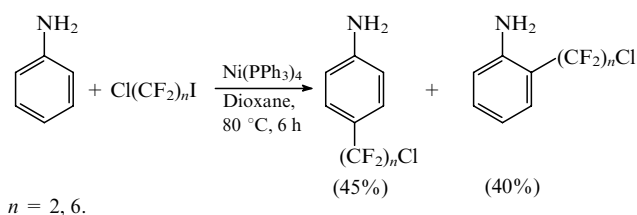
R = Me(CH₂)₅, MeO(CH₂)₂, HOCH₂, PhCH₂, HO(CH₂)₄, (EtO₂C)₂CHCH₂, Me₂CHCH₂; R_F = n-C₄F₉, n-C₆F₁₃.

It was found that the copper acetate—hydrazine hydrate system catalyses reactions of perfluoroalkyl iodides with alkenes and alkynes;³⁴⁰ the yields of the target products vary from 65% to 90%.

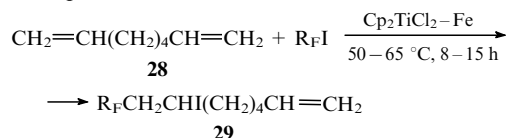


The KI—CuSO₄ system is also active in these reactions.³⁴¹ In the presence of this system, cupric perfluoroalkanesulfonates react with alkenes with the formation of addition products at the multiple bond, viz., R_FSO₂CH₂CHIR.

Nickel complexes effectively catalyse the perfluoroalkylation of aromatic compounds under the action of polyfluoroalkyl iodides.³⁴²

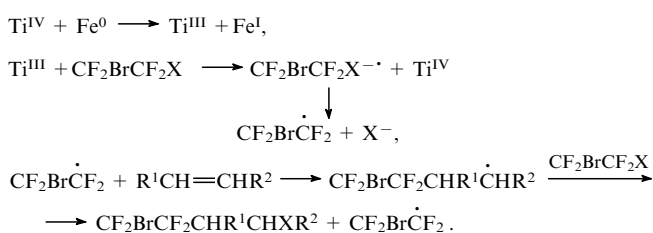


It was found³⁴³ that the Cp₂TiCl₂—Fe system catalyses the reactions of perfluoroalkyl iodides XCF₂CF₂I (X = Cl, Br) with alkenes and alkynes which yield 1 : 1 adducts.^{343–345} The use of octa-1,7-diene (**28**) as an alkene results in the involvement of only one multiple bond and the formation of the adduct **29**.

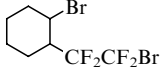
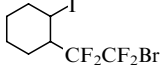
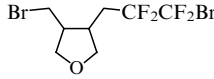
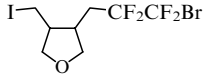


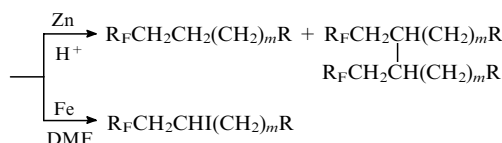
R_F = ClC₄F₈ (87%), C₄F₉ (88%), (CF₂)₂CF (92%), CF₂ClCF₂ (90%).

In the presence of 30 mol.-equiv. of Fe and 2 mol.-equiv. of Cp₂TiCl₂, 1,2-dihalogenotetrafluoroethane CF₂BrCF₂X (X = I, Br) reacts with alkenes in EtOH under a nitrogen atmosphere to give addition products in excellent yields (Table 12). The experimental results provide support for a radical mechanism of this reaction. In the perfluoroalkylation induced by CF₂BrCF₂X in the presence of Cp₂TiCl₂ as a catalyst, 2-bromotetrafluoroethyl radical can be formed, apparently according to the following scheme:^{346, 347}

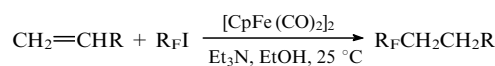


$$\text{CF}_2\text{BrCF}_2\text{X} + \text{R}^1\text{CH}=\text{CHR}^2 \longrightarrow \text{CF}_2\text{BrCF}_2\text{CHR}^1\text{CHXR}^2$$

Alkene	R _F X	T /°C	t /h	Product	Yield (%)
Oct-1-ene	CF ₂ BrCF ₂ I	55	10	CF ₂ BrCF ₂ CH ₂ CHIC ₆ H ₁₃	96
	CF ₂ BrCF ₂ I	25	15	CF ₂ BrCF ₂ CH ₂ CHIC ₆ H ₁₃	91
	CF ₂ BrCF ₂ Br	55	15	CF ₂ BrCF ₂ CH ₂ CHBrC ₆ H ₁₃	95
Hex-1-ene	CF ₂ BrCF ₂ Br	60	15	CF ₂ BrCF ₂ CH ₂ CHBrC ₄ H ₉	93
Hexa-1,5-diene	CF ₂ BrCF ₂ Br	60	26	CF ₂ BrCF ₂ CH ₂ CHBr(CH ₂) ₂ CH = CH ₂	78
Cyclohexene	CF ₂ BrCF ₂ Br	70	36		92
	CF ₂ BrCF ₂ I	65	24		92
Allyl alcohol	CF ₂ BrCF ₂ I	65	13	CF ₂ BrCF ₂ CH ₂ CHICH ₂ OH	96
Diallyl ether	CF ₂ BrCF ₂ Br	60	8		95
	CF ₂ BrCF ₂ I	55	7		94

$$\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}_2\text{CH}_3 + \text{R}_\text{F}\text{I} \xrightarrow[\text{Zn, THE, 20 }^\circ\text{C, 1 h}]{\text{Cp}_2\text{TiCl}_2} \text{R}_\text{F}\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$$
$$\text{CH}_2=\text{CH}(\text{CH}_2)_m\text{R} + \text{R}_\text{F}\text{I} \longrightarrow$$


The cyclopentadienyldicarbonyl iron dimer is yet another efficient catalyst of the reaction of perfluoroalkyl iodides with alkene derivatives.^{348, 349}


$$\text{CH}_2=\text{CHOEt} + \text{CF}_3(\text{CF}_2)_5\text{I} \xrightarrow[\text{Et}_3\text{N, EtOH, 25 } ^\circ\text{C}]{[\text{CpFe}(\text{CO})_2]_2} \text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2\text{OEt}$$

(63%–95%)

Successful perfluoroalkylation of alkenes containing electron-accepting substituents (*e.g.*, acrylates, acrylonitrile, methyl vinyl ketone, *etc.*) was carried out with Zn-bis(dimethylglyoximate)-pyridinecobalt(II) bromide [BrCo(dmgH)₂Py, **30**] in ethanol as a

$$\text{Cyclohexane ring with } \text{CF}_2\text{CF}_2\text{Br} \text{ and } \text{Br} \text{ substituents} + \text{CH}_2=\text{CHCO}_2\text{R} \xrightarrow[\text{EtOH, 20 } ^\circ\text{C, 24 h}]{\text{BrCo(dmgH)}_2\text{Py-Zn}} \text{Cyclohexane ring with } (\text{CF}_2)_2(\text{CH}_2)_2\text{CO}_2\text{R} \text{ and } \text{Br} \text{ substituents}$$

Zinc itself can exert a pronounced effect on the reactions of alkenes with perfluoroalkyl iodides. For example, the reaction of $\text{Me}(\text{CH}_2)_4\text{CH}=\text{CH}_2$ with $\text{CF}_3(\text{CF}_2)_3\text{I}$ yielded 90% of $\text{Me}(\text{CH}_2)_4\cdot\text{CHICH}_2(\text{CF}_2)_3\text{CF}_3$.³⁵¹

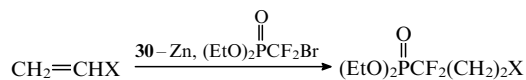
The system $\text{Co}-\text{Zn}$ was used for perfluoroalkylation of alkenes by perfluoroalkyl iodides and -bromides.^{256, 259, 344} Thus perfluoroalkylation of various cyclic, linear, symmetric or asymmetric alkenes with Freon-2402 (1,2-dibromo-1,1,2,2-tetrafluoroethane) resulted in derivatives containing a CF_2CF_2 fragment.^{354, 355} It may be noted that the activation of the $\text{C}-\text{Br}$ bond, *e.g.*, in $\text{RCF}_2\text{CF}_2\text{Br}$, by cobalt in the low valent state generated *in situ* occurs with high efficiency, which made it possible to induce reactions of these compounds with unsaturated substrates.²⁵⁹

Table 13. Perfluoroalkylation of alkenes by perfluoroalkyl iodides in the presence of the catalytic system **30** – Zn.³⁵⁴

Alkene	R _F X	T / °C	t / h	Product	Yield (%) (E : Z)
H ₂ C=CHCO ₂ Et	Cl(CF ₂) ₆ I	15	0.5	R _F CH ₂ CH ₂ CO ₂ Et	56
	F(CF ₂) ₄ I	20	0.5	R _F CH ₂ CH ₂ CO ₂ Et	71
	F(CF ₂) ₆ I	20	0.5	R _F CH ₂ CH ₂ CO ₂ Et	72
	F(CF ₂) ₈ I	20	0.5	R _F CH ₂ CH ₂ CO ₂ Et	75
	CF ₂ ClCF ₂ I ^a	65	10	R _F CH ₂ CH ₂ CO ₂ Et	92
	CF ₂ BrCF ₂ Br	75	11	R _F CH ₂ CH ₂ CO ₂ Et	93
	CF ₂ BrCFClBr	50	10	R _F CH ₂ CH ₂ CO ₂ Et	90
	CF ₂ Br ₂	70	24	R _F CH ₂ CH ₂ CO ₂ Et	90
H ₂ C=CHCN	Cl(CF ₂) ₄ I	30	2	R _F CH ₂ CH ₂ CN	61
	CF ₂ BrCF ₂ I	65	10	R _F CH ₂ CH ₂ CO ₂ Et	93
	C ₆ F ₁₃ I	30	2.5	R _F CH ₂ CH ₂ CN	71
	C ₈ F ₁₇ I	30	3	R _F CH ₂ CH ₂ CN	69
	C ₆ F ₁₃ Br	30	3.5	R _F CH ₂ CH ₂ CN	75
	C ₈ F ₁₇ Br	30	4	R _F CH ₂ CH ₂ CN	70
H ₂ C=CHC(O)Me	Cl(CF ₂) ₆ I	30	5	R _F CH ₂ CH ₂ C(O)Me	45
	C ₄ F ₉ I	25	4	R _F CH ₂ CH ₂ C(O)Me	49
	C ₆ F ₁₃ I	30	3.5	R _F CH ₂ CH ₂ C(O)Me	64
	C ₆ F ₁₃ Br	45	5	R _F CH ₂ CH ₂ C(O)Me	72
	C ₈ F ₁₇ Br	45	5	R _F CH ₂ CH ₂ C(O)Me	53
HC≡CCO ₂ Et	ClC ₄ F ₈ I	25	8	R _F CH=CHCO ₂ Et	85 (26 : 74)
	C ₄ F ₉ I	20	7	R _F CH=CHCO ₂ Et	73 (9 : 91)
	C ₆ F ₁₃ Br	30	7	R _F CH=CHCO ₂ Et	76 (30 : 70)
	C ₈ F ₁₇ Br	30	10	R _F CH=CHCO ₂ Et	65 (28 : 72)

^a The reaction was carried out in the presence of the catalytic system Cp₂TiCl₂ – Fe.

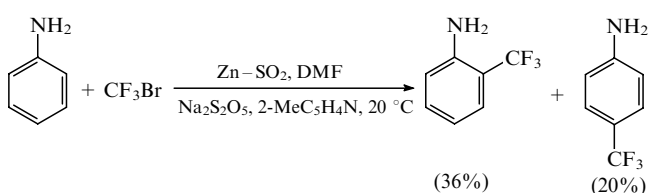
The (diethoxyphosphoryl)difluoromethyl group was successfully introduced into alkenes containing electron-withdrawing substituents by the reaction with (EtO)₂P(O)CF₂Br in the presence of the system **30** – Zn.^{344, 346–348}



X = CO₂Et, CO₂H, CN, CH₂Cl, CONH₂, COMe, OAc, OEt, CO₂Me, Buⁿ.

The yield of the reaction products increases after addition of 1 equiv. of HCOONH₄. Apparently, the surface of zinc is activated by ammonium ions. Other ammonium salts, *e.g.*, NH₄Cl, NH₄Br and NH₄OAc, can also be used for this purpose; however, the yields of the reaction products are lower.

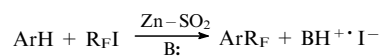
Reduction of commercial Freon-1301 (bromotrifluoromethane) to the trifluoromethyl radical possessing electrophilic character using the Zn – SO₂ system in DMF in the presence of Na₂S₂O₅ and bases (Na₂HPO₄, 2-methylpyridine) was a step forward on the way to trifluoromethylation of aromatic and heterocyclic compounds.^{138, 171, 267, 353, 355–357} Thus the reaction of CF₃Br with aniline in the presence of this system gives a mixture of *ortho*- and *para*-trifluoromethylanilines with the *ortho*-isomer prevailing.



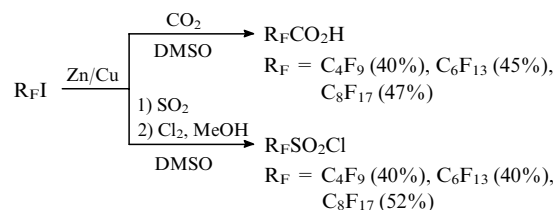
Trifluoromethylation of pyrrole and *N*-methylpyrrole occurs at position 2.

In the presence of this system, perfluoroalkyl iodides F(CF₂)_{*n*}I (*n* = 1, 2, 4, 6, 8) efficiently react with aromatic compounds

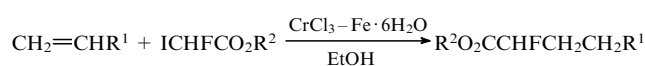
containing electron-donor substituents (phenols, anisole, anilines, aminophenols, toluene) and pyrrole.



The reaction of perfluoroalkyl iodides with CO₂ in the presence of the Zn/Cu couple in DMSO results in perfluorinated carboxylic acid, this presents special interest.^{358–360} An analogous reaction with SO₂ gives the corresponding perfluoroalkanesulfonyl chlorides.³⁶⁰



Some metal halides can effectively catalyse perfluoroalkylation reactions. Thus the redox system CrCl₃ – Fe in ethanol promotes the perfluoroalkylation of alkenes containing electron-withdrawing substituents^{256, 347, 361, 362} under the action of CF₂Br₂ (Table 14),²⁰⁵ CF₃Cl or ICHFCO₂R (R = Me, Et) at 60–70 °C.²⁸⁷



R¹ = CO₂Me (71%), CO₂Et (78%), CN (74%), COMe (75%);

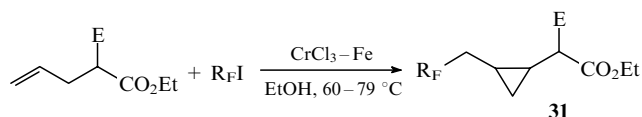
R² = Me, Et.

The CrCl₃ – Fe system is efficient in the reaction of perfluoroalkyl iodides Cl(CF₂)_{*n*}I (*n* = 2, 4, 6, 8), C₄F₉I, C₆F₁₃I and C₈F₁₇I with methyl α-acetylaminocrylate resulting in β-perfluoroalkyl-α-amino acid derivatives R_FCH₂CH(NHAc)CO₂Me in 65% to 80% yields. The reaction of perfluoroalkyl iodides with diethyl allylmalonate and its analogues in the presence of the CrCl₃ – Fe system gives perfluoroalkylmethyl-substituted derivatives of

Table 14. Reactions of alkenes containing electron-withdrawing substituents with CF₂Br₂ in the presence of the FeCrCl₃ system in EtOH.²⁰⁵

Alkene	<i>T</i> / °C	<i>t</i> / h	Product	Yield (%)
CH ₂ =CHCO ₂ Et	60	20	CF ₂ Br(CH ₂) ₂ CO ₂ Et	72
CH ₂ =CHCO ₂ Me	60	20	CF ₂ Br(CH ₂) ₂ CO ₂ Me	62
CH ₂ =C(Me)CO ₂ Et	60	24	CF ₂ BrCH ₂ CH(Me)CO ₂ Et	80
MeCH=CHCO ₂ Et	75	24	CF ₂ BrCH(Me)CH ₂ CO ₂ Et	43
CH ₂ =CHCO ₂ H	65	20	CF ₂ Br(CH ₂) ₂ CO ₂ H	64
CH ₂ =CHCONH ₂	70	20	CF ₂ Br(CH ₂) ₂ CONH ₂	72
CH ₂ =CHCN	60	18	CF ₂ Br(CH ₂) ₂ CN	62
CH ₂ =CHCOMe	60	20	CF ₂ Br(CH ₂) ₂ COMe	60
CH ₂ =CHBu ⁿ	60	10	CF ₂ BrCH ₂ CHBrBu ⁿ	96
CH ₂ =CHC ₆ H ₁₃ -n	60	10	CF ₂ BrCH ₂ CHBrC ₆ H ₁₃ -n	84
CH ₂ =CH(CH ₂) ₂ CH=CH ₂	60	6	CF ₂ BrCH ₂ CHBr(CH ₂) ₂ CH=CH ₂	72
CH ₂ =CH(CH ₂) ₂ Ac	60	13	CF ₂ BrCH ₂ CHBr(CH ₂) ₂ Ac	64
CH ₂ =CH(CH ₂) ₈ CO ₂ Me	60	8	CF ₂ BrCH ₂ CHBr(CH ₂) ₈ CO ₂ Me	64
CH ₂ =CHCH ₂ OAc	60	12	CF ₂ BrCH ₂ CHBrCH ₂ OAc	30
	12	8	CF ₂ BrCH ₂ CHBr(CH ₂) ₃ Me	74

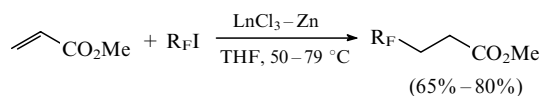
cyclopropane **31** in high yields.^{355, 356} Ethanol is the best solvent for this reaction.



R _F	E	Yield (%)	R _F	E	Yield (%)
C ₂ F ₅	CO ₂ Et	89	C ₆ F ₁₃	COMe	92
C ₆ F ₁₃	CO ₂ Et	92	C ₄ F ₉	CN	76
C ₈ F ₁₇	CO ₂ Et	85	C ₈ F ₁₇	CN	70
C ₄ F ₉	COMe	87	C ₆ F ₁₃	CN	69
C ₈ F ₁₇	COMe	85			

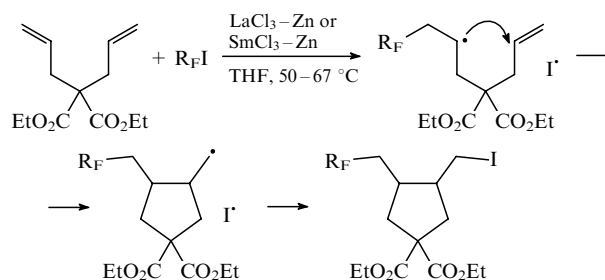
The YbCl₃–Zn and LnCl₃–Zn systems produce a similar effect.^{138, 251, 254, 256} Thus the reaction of perfluorohexyl iodide with CH₂=CHCH₂OAc in THF in the presence of the YbCl₃–Zn system results in F(CF₂)₆(CH₂)₃OAc in 95% yield. This can be explained by the fact that the primary addition product to the double bond undergoes reductive deiodination.

The efficiency of the YbCl₃–Zn system in catalytic reactions of perfluoroalkyl iodides with alkenes was studied (Table 15).^{250–256} This reaction is completed within several minutes in tetrahydrofuran but does not take place in EtOH or benzene.



The reaction of substituted hepta-1,6-diene with perfluoroalkyl iodide in the presence of the LaCl₃–Zn or SmCl₃–Zn system is accompanied by cyclisation involving the second double bond and results in a mixture of the corresponding *cis*- and *trans*-

3-iodomethyl-4-perfluoroalkylmethyl-1,1-di(ethoxycarbonyl)cyclopentanes (**4**: **1**).¹³⁸

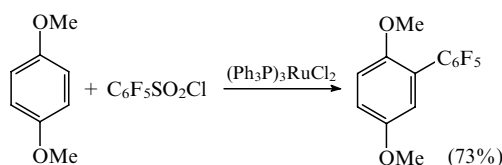


R_F = ClC₄F₈, ClC₆F₁₂, C₆F₁₃, C₈F₁₇.

The NiCl₂·6 H₂O–Zn system in THF proved to be efficient in the reaction of iodoacetates with alkenes resulting in δ-iodo esters in good yields.^{251–253} In the case of perfluoroalkyl chlorides, the hydrogen atom is substituted for chlorine.²⁵²

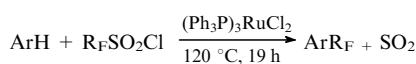
Activation of perfluoroalkyl iodides by transition metal complexes. Transition metal complexes can also efficiently activate perfluoroalkyl iodides.

Perfluoroalkanesulfonyl chlorides F(CF₂)_nSO₂Cl (*n* = 1–20) and pentafluorobenzenesulfonyl chloride can replace perfluoroalkyl iodides in perfluoroalkylation and arylation reactions of aromatic and heterocyclic compounds and alkenes with (Ph₃P)₃RuCl₂ as a catalyst.^{355, 363–367}

**Table 15.** Perfluoroalkylation of alkenes with perfluoroalkyl iodides in the presence of the YbCl₃/Zn system.²⁵¹

Alkene	R _F	Time / min	Product	Yield (%)
CH ₂ =CHCH ₂ OAc	F(CF ₂) ₆	6	F(CF ₂) ₆ (CH ₂) ₃ OAc	95
CH ₂ =CHCH ₂ OH	F(CF ₂) ₆	7	F(CF ₂) ₆ (CH ₂) ₃ OH	56
CH ₂ =CHCH ₂ P(O)(OEt) ₂	F(CF ₂) ₆	10	F(CF ₂) ₆ (CH ₂) ₃ P(O)(OEt) ₂	60
CH ₂ =CHC ₆ H ₁₃ -n	Cl(CF ₂) ₈	10	Cl(CF ₂) ₈ (CH ₂) ₂ C ₆ H ₁₃	58

Note: The alkene : R_FI : YbCl₃ : Zn molar ratio is 1.00 : 1.00 : 0.05 : 0.50.



R _f	Ar	Yield (%)	R _f	Ar	Yield (%)
CF ₃	Ph	41	C ₆ F ₁₃	Ph	44
CF ₃	MeC ₆ H ₄	36	C ₆ F ₁₃	MeC ₆ H ₄	54
CF ₃	MeOC ₆ H ₄	58	C ₆ F ₁₃	MeOC ₆ H ₄	59
CF ₃	1,4-Me ₂ C ₆ H ₃	63	C ₆ F ₁₃	1,4-Me ₂ C ₆ H ₃	41
C ₆ F ₁₃	1,4-(MeO) ₂ C ₆ H ₃	71			

The addition product to the double bond is formed in the reaction with alkenes.^{301, 368, 369}

This catalytic system was effective in perfluoroalkylation of arenes^{363, 364, 370, 371} and enol silyl ethers by perfluoroalkanesulfonyl chlorides (Table 16).³⁶⁶

Table 16. Reactions of aromatic compounds with pentafluorobenzenesulfonyl chloride in the presence of (Ph₃P)₃RuCl₂ at 240 °C.³⁶⁶

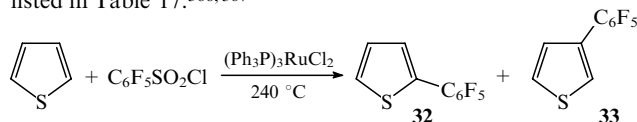
Substrate	Time /h	Product	Yield (%)
PhH	24	C ₆ F ₅ Ph	73
PhOMe	4	C ₆ F ₅ C ₆ H ₄ OMe ^d	14
PhCl	8	C ₆ F ₅ C ₆ H ₄ Cl ^b	87
PhCN	4	C ₆ F ₅ C ₆ H ₄ CN ^c	39
<i>p</i> -Me ₂ C ₆ H ₄	4	C ₆ F ₅ C ₆ H ₃ Me ₂	59
<i>p</i> -MeC ₆ H ₄ CHMe ₂	4	MeC ₆ H ₃ (C ₆ F ₅)CHMe ₂	14
<i>p</i> -(MeO) ₂ C ₆ H ₄	2	C ₆ F ₅ C ₆ H ₃ (OMe) ₂	5

^a The ratio of the *ortho* : *meta* : *para* isomers is 43 : 16 : 41.

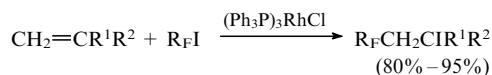
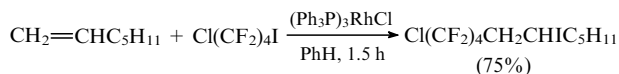
^b The ratio of the *ortho* : *meta* : *para* isomers is 42 : 31 : 27.

^c The ratio of the *ortho* : *meta* : *para* isomers is 27 : 43 : 30.

Perfluorophenylation of various thiophene derivatives by C₆F₅SO₂Cl in the presence of the (Ph₃P)₃RuCl₂ complex was studied under similar conditions. The results of these studies are listed in Table 17.^{366, 367}



Perfluoroalkyl iodides add to alkenes in the presence of the Wilkinson catalyst [tris(triphenylphosphine)rhodium chloride] at 80 °C.^{298, 372} This catalyst ensures high chemoselectivity under mild reaction conditions.



R_f = Cl(CF₂)₄, F(CF₂)₄, Cl(CF₂)₆, Cl(CF₂)₂;

R¹ = *n*-C₅H₁₁, *n*-C₆H₁₃, Buⁿ, Me₂CHCH₂, Et; R² = H, Me.

Perfluoroalkyl iodides R_fI [R_f = Cl(CF₂)₄, Cl(CF₂)₆, CF₃(CF₂)₃] react with alkenes and alkynes in the presence of Ir(H)(CO)(PPh₃)₃. The addition reaction to the triple bond yields predominantly *E*-isomers.³⁵⁸

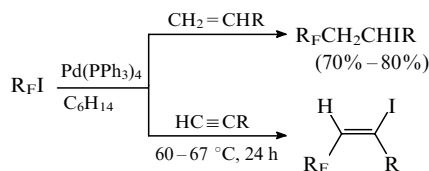
The perfluoroalkyl radical R_f• generated from perfluoroalkyl iodides in the presence of metals or transition metal complexes reacts smoothly with alkenes containing both electron-donor and electron-withdrawing substituents. As in the case of sulfonatode-

Table 17. Reactions of thiophene and its derivatives with pentafluorobenzenesulfonyl chloride in the presence of (Ph₃P)₃RuCl₂.³⁶⁶

Substrate	Product	Yield (%)
		22
		6
		14
		5
		7
		39
		17
		11

halogenation, these complexes effectively catalyse the addition of perfluoroalkyl halides to both types of alkenes.

Tetrakis(triphenylphosphine)palladium is also efficient in reactions of perfluoroalkyl iodides with alkenes and alkynes in hexane.^{278, 302, 305, 310, 373 - 376}



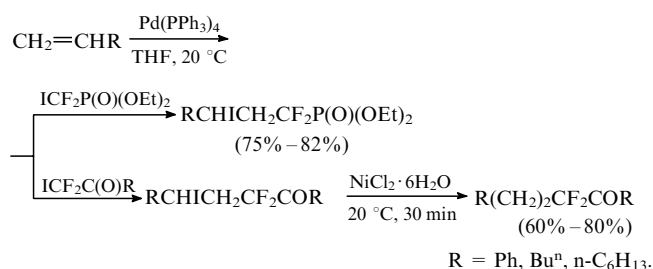
R_f = CF₃(CF₂)₃, CF₃(CF₂)₂, CF₃(CF₂)₅; R = (CH₂)₂OH, Ph, *n*-C₆H₁₃, SiMe₃, Buⁿ, CH₂SiMe₃, (CH₂)₂CO₂Me, CH₂OH.

For example, chlorododecafluorohexyl iodide reacts with hept-2-ene in the presence of 0.5 mol. % Pd⁰ (20 min, 20 °C) resulting in the addition product (yield 97%). An increase in temperature from 20 to 100 °C has little effect on this reaction.

The trialkylstannyl group at the carbon atom of the multiple bond can be replaced by the perfluoroalkyl group by treatment with perfluoroalkyl iodide in the presence of Pd(PPh₃)₄.³⁷⁷ Thus the reaction of (*E*)-PhCH=CHSnBu₃ with perfluorobutyl iodide in the presence of Pd(PPh₃)₄ in hexane with boiling for 4 min results in (*E*)-PhCH=CHC₄F₉ in 68% yield.^{297, 377}

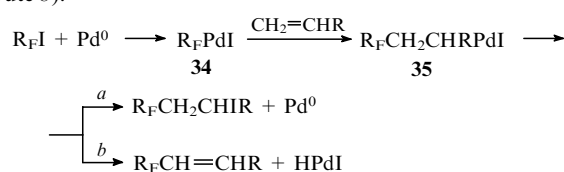
A mixture of *cis*- and *trans*-ethers R_fCH=CHOR (yields 51%–86%) is formed in the reaction of R_fI (R_f = CF₃, C₃F₇, C₆F₁₃) with CH₂=CHOR (R = H, Buⁿ) in hexane in the presence of Pd(PPh₃)₄ and Et₃N.³⁷⁸

α,α-Difluoro-substituted esters of carboxylic and phosphonic acids are prepared by the reaction of iodo-substituted derivatives of these acids with alkenes in the presence of Pd(PPh₃)₄. Subsequent treatment of the iodo-substituted derivative with NiCl₂·6 H₂O results in the formation of the reduction product.^{158, 250 - 256}



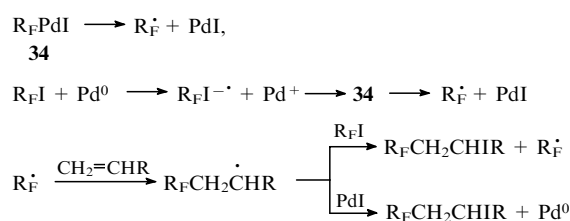
Zero-valent palladium also catalyses the reactions of aryl- or alkenyl halides with alkenes resulting in addition products.³⁷⁹

Most probably, the complex **34**, which is formed first, yields an organopalladium derivative **35** in reactions with alkene.³⁸⁰ Its further transformations can include reduction of palladium to Pd⁰ with the formation of an addition product to the multiple bond (route *a*) or elimination of the hydrogen atom from the β-position under the action of palladium eventually resulting in a new alkene (route *b*).



Palladium(0) is the only possible reagent in the formation of a radical anion of perfluoroalkyl iodide (reduction) which yields the perfluoroalkyl radical initiating further conversions. The formation of a cyclic system in the reaction of perfluoroalkyl iodide with diallyl ether in the presence of Pd⁰ provides strong evidence in favour of the radical mechanism of this reaction.

On the other hand, this reaction may occur *via* the generation of the perfluoroalkyl radical upon decomposition of the complex **34**. The perfluoroalkyl radical further reacts with alkene to give the target product.



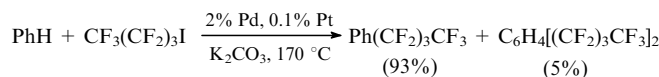
The EPR spectra of perfluoroalkyl radicals generated in these reactions could not be recorded because of their high reactivity and low concentration.²⁷⁸ However, the use of *N*-benzylidene-*tert*-butylamine *N*-oxide as a spin trap made it possible to obtain well-resolved EPR spectra in which the trapped [Cl(CF₂)₄][•] radical could be detected as the radical [Cl(CF₂)₄CH(Ph)N(O[•])Bu^t].²⁷⁸ These findings provide evidence both for the electron transfer in this reaction and the oxidation of Pd⁰ by perfluoroalkyl iodide resulting in the formation of a perfluoroalkyl palladium complex of the type **34** as occurring with the formation of a transient radical.

Fluorine-containing aliphatic mono- and dicarboxylic acids were obtained by the reaction of perfluoroalkyl iodides or -bromides with CO₂ in the presence of the Group VIII transition metal complexes and subsequent hydrolysis of the reaction products.^{381, 382} Thus CF₃(CF₂)₇CO₂H was isolated in 40% yield upon hydrolysis of the reaction product of CF₃(CF₂)₇I with CO₂ in DMF in an autoclave in the presence of Pd(PPh₃)₄ at 60 °C. This suggests the intermediate formation of the perfluoroalkyl radical which further reacts with carbon dioxide.

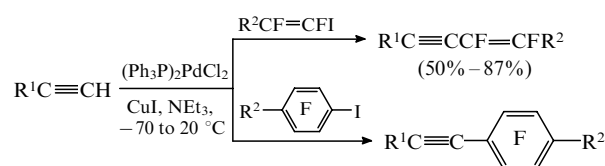
When the reaction is carried out in the presence of alkenes and a CO₂ source, the intermediate radical formed as the product of addition of the perfluoroalkyl radical to the multiple bond reacts further with CO₂ to yield a carboxylic acid. With alcohol as a solvent, this reaction gives the corresponding ester. Thus the

reaction of hex-1-ene with C₈F₁₇I in the presence of K₂CO₃ and dichlorobis(triphenylphosphine)palladium in ethanol (12 h, 80 °C) gives C₈F₁₇CH₂CHBuCO₂Et in 67% yield.^{383, 384}

Perfluoroalkylation of aromatic compounds by perfluoroalkyl iodides can be carried out in the presence of zero-valent transition metals (*e.g.*, Rh, Pd, Pt, Ru, Cu, Ni, Re) and aqueous K₂CO₃.³⁸⁵ The yields of disubstituted products are usually low.

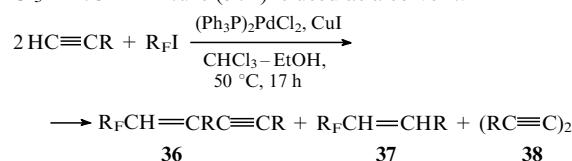


On the other hand, the reaction of perfluorovinyl- and polyfluoroaryl iodides with alkynes in the presence of the (Ph₃P)₂PdCl₂–CuI complex results in the formation of addition products to the triple bond and elimination of HI.^{361, 373–376}



R¹ = OMe, NMe₂, F, Br; R² = (CH₂)_{*n*}Me (*n* = 3–6), Ph, (CH₂)₃CN, CH₂Oph, CH₂OH, CH(OH)Me.

The reaction of perfluoroalkyl iodides with alkynes in the presence of a palladium catalyst and bases (*e.g.*, K₂CO₃, Et₃N) yields mixtures of enynes and alkenes.³⁸⁶ The co-catalyst CuI increases the yield of enynes. The best results are attained when the CHCl₃–EtOH mixture (5 : 1) is used as a solvent.



R _F	R	Yield (%)		
		36	37	38
n-C ₈ F ₁₇	Bu ⁿ	74	3	7
n-C ₃ F ₇	SiMe ₃	70	—	—

These reactions occur smoothly without complications and allow for high variability of functional groups without resorting to the use of toxic or hazardous reagents.

Palladium derivatives efficiently catalyse the reactions of perfluoroalkyl halides with allylic alcohols which occur in the presence of K₂CO₃ and result in the formation of polyfluoroalkyl-substituted oxiranes (Table 18).³⁸⁶

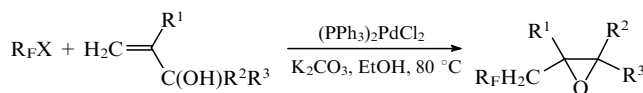
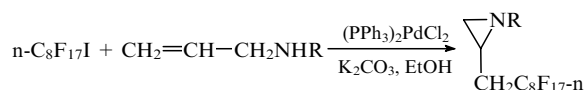


Table 18. Reactions of allylic alcohols H₂C=CR¹C(OH)R²R³ with perfluoroalkyl iodides R_FI in EtOH in the presence of (Ph₃P)₂PdCl₂.³⁸⁶

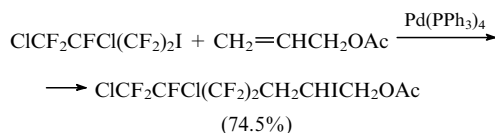
R ¹	R ²	R ³	R _F	Yield of oxirane (%)
H	H	H	n-C ₈ F ₁₇	70
H	H	Me	n-C ₈ F ₁₇	71
H	Me	Me	n-C ₈ F ₁₇	79
H	H	n-C ₆ H ₁₃	CF ₃	63
H	H	n-C ₆ H ₁₃	C ₂ F ₅	71
H	H	n-C ₆ H ₁₃	n-C ₃ F ₇	77
H	H	n-C ₆ H ₁₃	n-C ₄ F ₉	72
H	H	n-C ₆ H ₁₃	n-C ₆ F ₁₃	74
H	H	n-C ₆ H ₁₃	CF ₂ ClCFCl	56

Similarly, perfluorooctylmethyl-substituted aziridines are obtained in the reaction of perfluorooctyl iodide with allylamines under identical conditions.

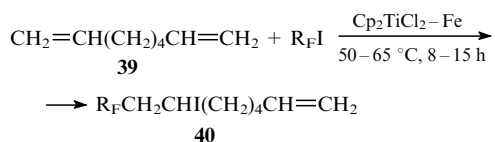


R = H (35%), Ph (41%).

On the other hand, the addition product to the multiple bond is formed in the reaction of perfluoroalkyl halides with allyl acetate in the presence of $\text{Pd}(\text{PPh}_3)_4$.³⁸²



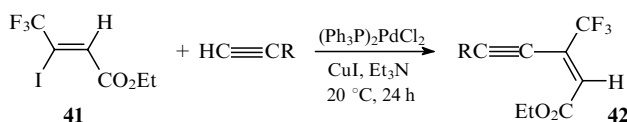
It was found³²⁸ that the dichlorobis(η -cyclopentadienyl)titanium(IV)–iron system efficiently catalyses the reactions of perfluoroalkyl iodides and -bromides with octa-1,7-diene (**39**). This reaction gives addition products to one multiple bond (**40**).



R_F = ClC₄F₈ (87%), C₄F₉ (88%), (CF₂)₂CF (92%), CF₂ClCF₂ (90%), CF₂BrCF₂ (91%), CF₂ClCFCl (81%).

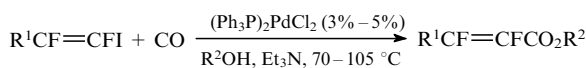
The Cp₂TiCl₂–Zn system is also efficient in reactions of allyl bromide with carbonyl compounds.³²⁹

Ethyl-4,4,4-trifluoro-3-iodo-(Z)-crotonate (**41**) is a valuable synthon in the synthesis of compounds containing the trifluoromethyl group. The reaction of alkynes with the ester **41** in the presence of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ results in compound **42** which contains a conjugated system of double and triple bonds in addition to the CF₃ group.^{387, 388}



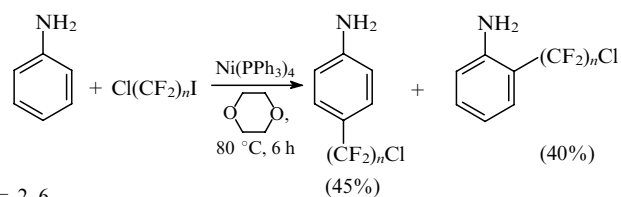
R = SiMe₃ (76%), Ph (87%), (CH₂)₇Me (92%), 4-MeOC₆H₄ (93%), 4-NO₂C₆H₄ (88%), (CH₂)₅Me (93%), (CH₂)₃Me (91%).

The reaction of (*E*)- and (*Z*)-1,2-difluoro-1-iodoalkenes and (*E*)- and (*Z*)- α,β -difluoro- β -iodostyrenes with carbon monoxide in the presence of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ as the catalyst, an alcohol and trialkylamine on heating yields carboxylic acid esters.³⁸⁹



Con- figura- tion	R ¹	Product	T / °C	Yield (%)
Z	Bu ^t	(<i>E</i>)-Bu ^t CF=CFCO ₂ Bu	105	85
Z	Bu ^s	(<i>E</i>)-Bu ^s CF=CFCO ₂ Bu	105	92
Z	Ph	(<i>E</i>)-PhCF=CFCO ₂ Bu	105	89
E	Bu ⁿ	(<i>Z</i>)-Bu ⁿ CF=CFCO ₂ Et	95	82
Z	4-MeOC ₆ H ₄	(<i>E</i>)-4-MeOC ₆ H ₄ CF=CFCO ₂ Bu	80	86
Z	4-CNC ₆ H ₄	(<i>E</i>)-4-CNC ₆ H ₄ CF=CFCO ₂ Bu	80	96
Z	4-CF ₃ C ₆ H ₄	(<i>E</i>)-4-CF ₃ C ₆ H ₄ CF=CFCO ₂ Bu	80	89
E	4-MeOC ₆ H ₄	(<i>Z</i>)-4-MeOC ₆ H ₄ CF=CFCO ₂ Bu	70	86

Nickel complexes also efficiently catalyse perfluoroalkylation of aromatic compounds.³⁴²



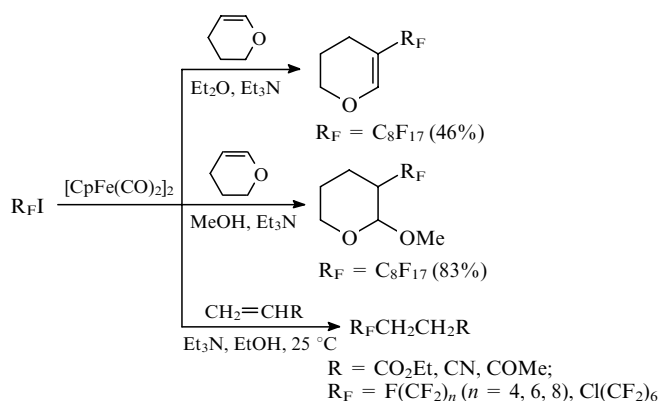
The search for novel methods for the synthesis of fluoroorganic compounds was based on the use of accessible carbonyls of zero-valent metals. It was found that carbonyl complexes of the Group VIII transition metals can efficiently catalyse the reaction of R_FI with alkenes and alkynes.^{180, 382, 383} For example, perfluoroalkyl iodides react with phenylacetylene in the presence of transition metal carbonyls, e.g., Ni(CO)₂(PPh₃)₃, resulting in β -perfluoroalkylstyrenes (yield 89%–96%) (Table 19).

Table 19. Reactions of phenylacetylene with perfluoroalkyl iodides.¹⁸⁰

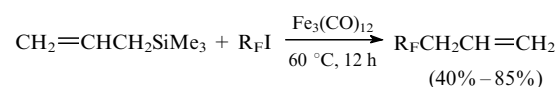
Catalyst	T / °C	t / h	Conver- sion (%)	Yield (%)
Ru/C	120	12	98.6	93
Pt/C	100	12	99.8	94
Ag/Al ₂ O ₃	125	11	99.7	94.5
Ni(CO) ₂ (PPh ₃) ₃	70	6	100	96
W(CO) ₅ [P(OEt) ₃]	90	5	95.7	89
Mo(CO) ₅ (PPh ₃)	80	5	97.9	92

Depending on the reaction conditions, iron pentacarbonyl converts the primary perfluoroalkyl iodide into 1-iodoperfluoroalk-1-ene or to a perfluoroalkyl radical which both can further perfluoroalkylate aromatic compounds and alkenes.^{233, 390, 391} The addition of I(CF₂)₄I to CH₂=CH₂ in the presence of Fe(CO)₅ and HOCH₂CH₂NH₂ in an autoclave at 100 °C results in ICH₂CH₂(CF₂)₄CH₂CH₂I (yield 78%).

Perfluoroalkyl iodides enter into addition or substitution reactions with alkenes^{346, 348} and dihydropyran³⁴⁸ in the presence of [CpFe(CO)₂]₂.

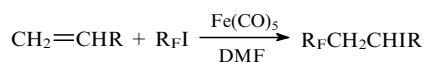


The reactions of trialkylsilyl derivatives of alkenes with perfluoroalkyl iodides in the presence of iron carbonyl, Fe₃(CO)₁₂ result in the substitution of the perfluoroalkyl group for the trialkylsilyl group.^{392, 393}



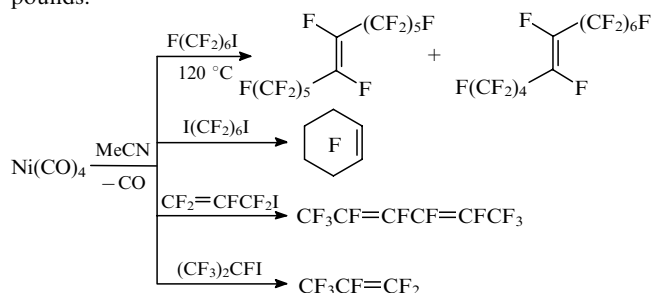
R_F = n-C₃F₇, n-C₈F₁₇, CF₂CF₂Br, CFCF₂Br, CFCF₂Cl, CHF₂CF₂Cl.

In the presence of Fe(CO)₅ in DMF, alkenes react with R_FI with the formation of addition products to the double bond.²⁸¹

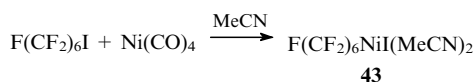


$\text{R}_\text{F} = (\text{CF}_3)_2\text{CFCF}=\text{CFCF}_2, \text{NCCF}_2, \text{MeCO}_2\text{CF}_2, \text{C}_3\text{F}_7, \text{CF}_3(\text{CF}_2)_4\text{CF}_2, \text{FSO}_2\text{CF}_2\text{CF}_2, (\text{CF}_3)_2\text{CFOCF}_2\text{CF}_2$; $\text{R} = \text{Bu}^\text{n}, \text{CO}_2\text{Me}$.

It was shown³⁹⁴ that nickel carbonyls are efficient in the reaction of substitution of the perfluoroalkyl group of α -chloro-fluoroketones for chlorine. When these reactions are carried out in donor solvents, organometallic compounds possessing perfluoroalkylating properties can be formed. For example, the reaction of perfluoroalkyl iodides with nickel tetracarbonyl in acetonitrile at 25–60 °C yields either dimeric products or unsaturated compounds.³⁹²



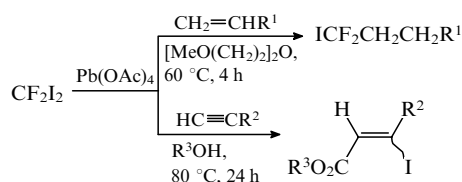
This reaction probably occurs *via* the intermediate formation of the nickel-containing compound **43**.



The reaction of perfluoroalkyl iodide with nickel tetracarbonyl is exothermic. The nickel compound formed reacts with the original substrate to give an isomeric mixture of perfluorohexa-2,4-diene. The reaction of perfluorohexyl iodide with nickel tetracarbonyl carried out at temperatures > 120 °C yields a mixture of two dodecenes, *viz.*, *trans*-perfluorododec-6-ene and *trans*-perfluorododec-5-ene (1 : 1) and perfluorocyclohexene.

2. Reactions of perfluoroalkyl halides with unsaturated organic compounds in the presence of redox systems

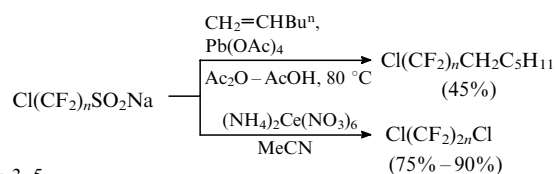
Studies of reactions of perfluoroalkyl halides with unsaturated organic compounds in the presence of reducing and oxidising systems revealed many specific features in their behaviour which can be rationalised by generation of perfluoroalkyl radicals. These radicals can be formed in different ways, predominantly by the reduction of perfluoroalkyl iodide to the radical anion. Hence a question arises as to whether the radical $\text{R}_\text{F}\cdot$ can be generated by an alternative route. According to some data, the reaction of perfluoroalkyl iodides with alkenes can be efficiently initiated by some oxidants, *e.g.*, $\text{Pb}(\text{OAc})_4$, $(\text{NH}_4)_2\text{S}_2\text{O}_8 - \text{HCO}_2\text{Na}$, $\text{CrCl}_3 - \text{Fe}$. Thus lead tetraacetate initiates the reaction of diiododifluoromethane with alkenes and alkynes.³⁹⁵



$\text{R}^1 = (\text{CH}_2)_3\text{Me}$ (95%), CH_2OH (93%), SiMe_3 (95%), CH_2OEt (92%), $(\text{CF}_2)_4\text{Cl}$ (80%), $(\text{CF}_2)_4\text{Br}$ (78%);
 $\text{R}^2 = \text{Bu}^\text{n}$; $\text{R}^3 = \text{Bu}^\text{n}$ (72%), Et (78%); $\text{R}^2 = \text{C}_5\text{H}_{11}$, $\text{R}^3 = \text{Et}$ (76%);
 $\text{R}^2 = \text{CH}_2\text{OMe}$; $\text{R}^3 = \text{Bu}^\text{n}$ (70%), Me (64%).

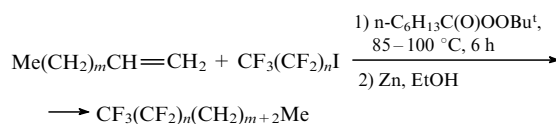
In addition to perfluoroalkyl iodides, these reactions occur with sodium perfluoroalkanesulfonates. For example, heating of $\text{Cl}(\text{CF}_2)_n\text{SO}_2\text{Na}$ with hex-1-ene in $\text{Ac}_2\text{O} - \text{AcOH}$ in the presence of $\text{Pb}(\text{OAc})_4$ at 80 °C results in the formation of an addition

product to the multiple bond, *viz.*, $\text{Cl}(\text{CF}_2)_n\text{CH}_2\text{C}_5\text{H}_{11}$, in 45% yield.³⁹⁶



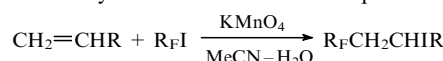
$n = 3, 5$.

Some peroxides are effective in reactions of perfluoroalkyl iodides with alkenes.³⁹⁷



$n = 1-21$; $m = 3-25$.

Potassium permanganate can also initiate the reaction of perfluoroalkyl iodides with alkenes in aqueous MeCN at 80 °C.³⁹⁸



$\text{R}_\text{F} = \text{Cl}(\text{CF}_2)_4, \text{Cl}(\text{CF}_2)_6$; $\text{R} = \text{Bu}^\text{n}, \text{CH}_2\text{OH}, \text{n-C}_6\text{H}_{13}, \text{n-C}_{10}\text{H}_{21}, \text{Me}_3\text{Si}, \text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2, \text{n-C}_{14}\text{H}_{29}$.

Some salts of Ce^IV efficiently induce perfluoroalkylation by perfluoroalkyl iodides. In the presence of $\text{Ce}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$ or $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, perfluoroalkyl halides $\text{R}_\text{F}\text{X}$ [$\text{R}_\text{F} = \text{Cl}(\text{CF}_2)_n$ ($n = 4, 6$), $\text{F}_3\text{C}(\text{CF}_2)_5$, $\text{X} = \text{I}$; $\text{R}_\text{F} = \text{CF}_2\text{Br}$, $\text{X} = \text{Br}$] react smoothly with alkenes $\text{RCH}=\text{CH}_2$ ($\text{R} = \text{Bu}^\text{n}, \text{CH}_2\text{OH}, \text{n-C}_8\text{H}_{17}$, *etc.*) (Tables 20 and 21) and alkynes to give perfluoroalkylation products.^{398, 399}

Table 20. The effect of the solvent on the reaction of but-1-ene and hex-1-ene with $\text{Cl}(\text{CF}_2)_4\text{I}$ and $\text{Cl}(\text{CF}_2)_6\text{I}$ in the presence of $\text{Ce}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$.³⁹⁸

Solvent	Conversion (%)		Yield (%)	
	A	B	C	D
DMF	100	100	81	82
MeOH	95	100	78	80
DMF – MeOH	50	60	31	38
DMSO	45	40	34	30
AcOH	0	0	0	0
$[\text{MeO}(\text{CH}_2)_2]_2\text{O}$	0	0	0	0

Note: A is $\text{Cl}(\text{CF}_2)_4\text{I}$, B is $\text{Cl}(\text{CF}_2)_6\text{I}$, C is $\text{RCHICH}_2(\text{CF}_2)_4\text{Cl}$, D is $\text{RCHICH}_2(\text{CF}_2)_6\text{Cl}$.

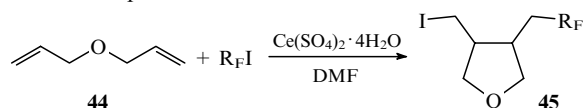
Table 21. The reaction of alkenes $\text{RCH}=\text{CH}_2$ with perfluoroalkyl halides $\text{R}_\text{F}\text{X}$ in the presence of $\text{Ce}(\text{SO}_4)_2 \cdot 4 \text{H}_2\text{O}$ in DMF.³⁹⁸

R	Yields for different $\text{R}_\text{F}\text{X}$ (%)			
	$\text{Cl}(\text{CF}_2)_4\text{I}$	$\text{Cl}(\text{CF}_2)_6\text{I}$	$\text{CF}_3(\text{CF}_2)_5\text{I}$	CF_2Br_2
Bu^n	81	73	84	83
CH_2OH	73	74	56	—
$\text{n-C}_6\text{H}_{13}$	82	85	82	86
$\text{n-C}_8\text{H}_{17}$	84	78	84	—
$\text{n-C}_9\text{H}_{19}$	84	81	—	86
$\text{n-C}_{10}\text{H}_{21}$	80	83	—	79
Me_3Si	68	—	—	—
$\text{CH}_2\text{OCH}=\text{CH}_2$	65	81	—	83
$\text{n-C}_{14}\text{H}_{29}$	78	—	—	—

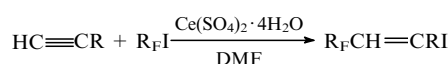
Note. The reaction was carried out at 80 °C for 8 h (100% conversion).

In the presence of $\text{Mn}(\text{OAc})_3 \cdot 2 \text{H}_2\text{O}$ or $\text{Ce}(\text{SO}_4)_2$, sodium polyfluoroalkanesulfonates can be used in these reactions instead of perfluoroalkyl iodides. In this case, the perfluoroalkyl radical formed reacts with aromatic compounds⁴⁰⁰ and alkenes,²⁵⁰ which results in the formation of either substitution products of the hydrogen atom in the benzene ring or in the formation of adducts to the multiple bond. This approach was used for introducing perfluoroalkyl groups into the benzene rings of benzocrown ethers under the action of sodium perfluorosulfonates.⁴⁰¹

Tetrahydrofuran **45** derivatives (see Table 21) were prepared using diallyl ether (**44**) as a substrate; this reaction resulted in the formation of a free radical intermediate as could be evidenced from the EPR spectra.²³⁴



Reactions of perfluoroalkyl iodides with alkynes in the presence of Ce^{IV} salts (Table 22) proceed at a higher temperature (120 °C) and are slower (the reaction time varies from 18 to 20 h) than the corresponding reactions with alkenes.^{398, 399}



$\text{R}_\text{F} = \text{Cl}(\text{CF}_2)_4, \text{Cl}(\text{CF}_2)_6, \text{CF}_3(\text{CF}_2)_5;$

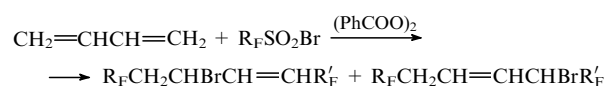
$\text{R} = \text{Bu}^n, \text{Ph}, n\text{-C}_6\text{H}_{13}, n\text{-C}_7\text{H}_{15}, \text{CH}_2\text{OH}, \text{MeOCH}_2.$

Table 22. The reaction of acetylene derivatives $\text{HC}\equiv\text{CR}$ with $\text{Cl}(\text{CF}_2)_4\text{I}$ and $\text{Cl}(\text{CF}_2)_6\text{I}$ in the presence of Ce^{IV} salts in DMF.³⁹⁸

R	Inducer	Yield of $\text{RFCH}=\text{CRI}$ (%) (<i>E</i> : <i>Z</i>)	
		$\text{Cl}(\text{CF}_2)_4$	$\text{Cl}(\text{CF}_2)_6$
Bu^n	$\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	73 (3 : 1)	71 (1 : 1)
Ph	$\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	55 (3 : 1)	74 (11 : 1)
	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	53 (6 : 1)	78 (5 : 1)
$n\text{-C}_6\text{H}_{13}$	$\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	68 (3 : 1)	—
	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	52 (4 : 1)	—
$n\text{-C}_7\text{H}_{15}$	$\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	59 (4 : 1)	76 (3 : 1)
	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	61 (6 : 1)	71 (5 : 1)
CH_2OH	$\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	48 (10 : 1)	65 (65 : 0)
	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	—	67 (9 : 1)
CH_2OMe	$\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	48 (2 : 5)	—

Note. The reaction was carried out at 120 °C for 18–20 h.

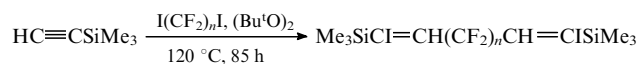
Butadiene undergoes perfluoroalkylation under the action of perfluoroalkanesulfonyl bromide $\text{R}_\text{F}\text{SO}_2\text{Br}$ in the presence of dibenzoyl peroxide to give a mixture of isomeric unsaturated addition products.⁴⁰²



$\text{R}_\text{F}, \text{R}'_\text{F} = \text{Cl}(\text{CF}_2)_4, \text{Cl}(\text{CF}_2)_5, \text{F}(\text{CF}_2)_5.$

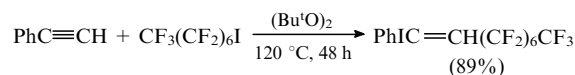
Dibenzoyl peroxide can also be used for perfluoroalkylation of aromatic compounds.²⁶⁸

The use of hydrogen peroxide, di-*tert*-butyl peroxide and dibenzoyl peroxide as inducers gave encouraging results. Thus the reaction of trimethylsilylacetylene with 1,6-diiodoperfluorohexane in the presence of di-*tert*-butyl peroxide results in 1,10-diiodo-1,10-bis(trimethylsilyl)dodecafluorodeca-1,9-diene in 92% yield.⁷⁰



$n = 6, 8, 10, 12.$

Treatment of phenylacetylene with perfluoroheptyl iodide in the presence of di-*tert*-butyl peroxide results in (*E*)-1-iodo-1-phenylpentadecafluoronon-1-ene.⁷⁰

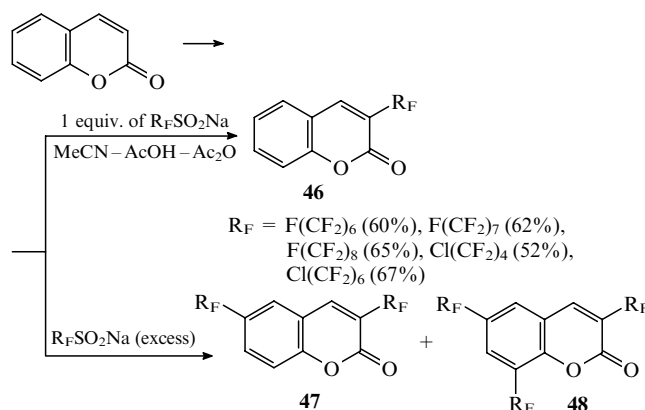


The reaction of alkenes with perfluoroalkyl iodides in the presence of hydrogen peroxide in acetone, acetonitrile or ethanol gives addition products to the multiple bond in good yields.⁴⁰³

Potassium superoxide (KO_2) reacts with 1,4-diiodoperfluorobutane in benzene containing dicyclohexano-18-crown-6 (its role in this reaction is ambiguous) to give $\text{I}(\text{CF}_2)_3\text{CO}_2\text{H}$.^{404, 405}

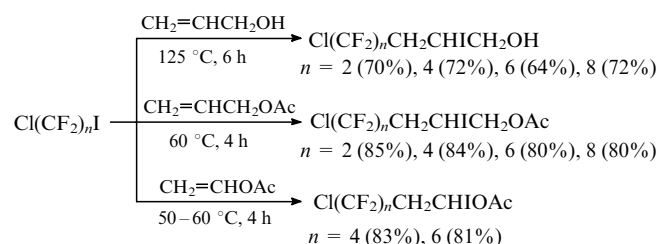
Sodium perfluoroalkanesulfonates of the type $\text{Cl}(\text{CF}_2)_n\text{SO}_2\text{Na}$ ($n = 4, 6, 8$) the reduction potentials of which are equal to 0.95–1.00 V generate perfluoroalkyl radicals in the presence of oxidants, e.g., $\text{Mn}(\text{OAc})_3 \cdot 2 \text{H}_2\text{O}$, $\text{Ce}(\text{SO}_4)_2$, HgSO_4 and Co_2O_3 .^{250–256} The radicals formed react with aromatic compounds to give monoperfluoroalkylation products. For example, the reaction of 1,4-dimethoxybenzene with $\text{Cl}(\text{CF}_2)_4\text{SO}_2\text{Na}$ in the presence of $\text{Mn}(\text{OAc})_3$ in H_2O , MeCN or AcOH at 80 °C gave the adduct 1,4-(MeO)₂ $\text{C}_6\text{H}_3(\text{CF}_2)_4\text{Cl}$ -2 in 50% yield.⁴⁰⁶

The reaction of sodium perfluoroalkanesulfonates with coumarin gives the 3-perfluoroalkyl derivatives **46**,²⁵⁷ 3,6-bis(perfluoroalkyl)- (**47**) and 3,6,8-tris(perfluoroalkyl) derivatives (**48**) are formed when the perfluoroalkylating reagent is used in excess. These compounds have found applications as fluorescent dyes and for laser systems.



The reaction of perfluoroalkyl iodides $\text{R}_\text{F}\text{I}$ [$\text{R}_\text{F} = \text{CF}_3(\text{CF}_2)_5, \text{H}(\text{CF}_2)_4, \text{Cl}(\text{CF}_2)_n$ ($n = 4, 6, 8$), $\text{I}(\text{CF}_2)_m$ ($m = 4, 6$), $\text{NaO}_3\text{S} \cdot (\text{CF}_2)_2\text{O}(\text{CF}_2)_m$ ($m = 2, 4$)] with NaHSO_3 in the presence of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ in aqueous acetonitrile at 70 °C results in the salts $\text{R}_\text{F}\text{SO}_2\text{Na}$ in 70% to 88% yields.¹⁵⁶

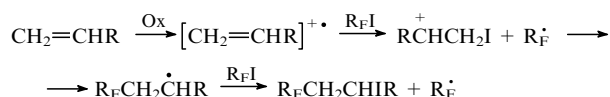
The $\text{Ce}^{\text{IV}} - \text{NaHCO}_3$ and $\text{Fe}^{\text{III}} - \text{NaHSO}_3$ systems efficiently catalyse the reactions of perfluoroalkyl iodides with alkenes. These reactions give high yields of addition products to the double bond.^{353, 407} $\text{K}_2[\text{Fe}(\text{CN})_6]$ was found to be an excellent inducer of reactions of addition of perfluoroalkyl iodides to alkenes and their derivatives.²⁴⁴



Let us now discuss the tentative reaction mechanisms underlying reactions of perfluoroalkyl halides and sodium perfluoroalkanesulfonates with unsaturated compounds in the presence of redox systems. These reactions were surveyed by Hu *et al.*³⁰

Two schemes are probable. According to the first of them, a radical cation is generated from perfluoroalkyl iodide under the action of an oxidant and is transformed to a perfluoroalkyl radical. The second route includes initial oxidation of the unsaturated substrate to the radical cation, which then reacts with perfluoroalkyl iodide to produce the perfluoroalkyl radical.

The latter was proposed by Huang and Xie⁴⁰⁰ for the reaction with styrene in the presence of lead tetraacetate.



Ox, oxidant.

However, standard oxidation potentials (E°_{ox}) of the alkenes used are too high to ensure their oxidation to the corresponding radical cations. For instance, E°_{ox} of oct-1-ene is 2.70 V relative to $\text{Ag}^+/\text{AgNO}_3$,⁴⁰⁸ although polar effects can to certain degree compensate for this stability.

An alternative intermediate, *viz.*, the radical cation of perfluoroalkyl iodide $[\text{R}_\text{F}\text{I}]^{\cdot+}$, can be formed under the action of a strong oxidant. Indeed, the same radical cation is formed in the electrochemical⁴⁰⁹ oxidation of perfluoroalkyl iodide in the presence of perfluoroalkanesulfonic acid.

Efficient catalysis of the reaction of perfluoroalkyl iodide with alkenes [*e.g.*, E°_{ox} of $\text{MeOC}_6\text{H}_4\text{C}(\text{Me})=\text{CH}_2$ is 1.49 V (see Ref. 410), E°_{ox} of α -phenylstyrene is 1.22 V relative to SCE⁴¹¹] requires an oxidant with a reduction potential, E°_{ox} , of > 1.6 V (rel. SCE). In this case, the radical cation $[\text{R}_\text{F}\text{I}]^{\cdot+}$ can be formed. The radical cation $[\text{R}_\text{F}\text{I}]^{\cdot+}$ is rapidly decomposed into $\text{R}_\text{F}^{\cdot}$ and the iodonium cation. The radical $\text{R}_\text{F}^{\cdot}$ was detected in its reaction with alkene, which resulted in the generation of a new radical. The latter detached iodine from $\text{R}_\text{F}\text{I}$ to yield the reaction product and the radical $\text{R}_\text{F}^{\cdot}$.

The reduction potentials of some oxidants are listed in Table 23.^{412,413} If the reduction potential of an oxidant is ≥ 1.60 V (rel. SCE), this can efficiently initiate the reaction with alkenes.

Table 23. Standard reduction potentials (E°_{red}) of different oxidants.

Oxidant	Ion	$E^\circ_{\text{red}}/\text{V}$	Ref.
$\text{Na}_2\text{S}_2\text{O}_8$, $(\text{NH}_4)_2\text{S}_2\text{O}_8$	$\text{S}_2\text{O}_8^{2-}$	2.01	412
KMnO_4	MnO_4^-	1.695	412
$\text{Pb}(\text{OAc})_4$, PbO_2	Pb^{4+}	1.69	412
$\text{Ce}(\text{SO}_4)_2$, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	Ce^{4+}	1.61	412
$\text{Mn}_2(\text{OAc})_3$	Mn^{3+}	1.51	412
$\text{K}_2\text{Cr}_2\text{O}_7$	$\text{Cr}_2\text{O}_7^{2-}$	1.33	412
FeCl_3	Fe^{3+}	0.771	412
Chloranil		0.02	413
$[\text{N}(\text{C}_6\text{H}_3\text{Br}_2-2,4)_3]^+$		1.14	413
$[\text{N}(\text{C}_6\text{H}_4\text{Br}-3)_3]^+$		0.70	413
$[\text{C}_6\text{H}_4\text{Br}-4]_3\text{N}^+$		1.06	414

Thus, the reactions of perfluoroalkyl halides with alkenes or alkynes in the presence of oxidants appear to be a convenient method for fluoroalkylation of alkenes or alkynes.

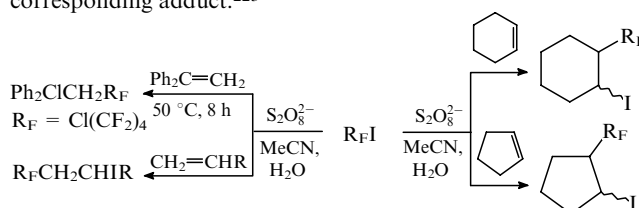
Perfluoroalkyl iodides successfully react with alkenes in aqueous MeCN (6–8 h, 60 °C) in the presence of $\text{Na}_2\text{S}_2\text{O}_8$ or $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Table 24).³⁹⁸ Cyclohexene and cyclopentene also react with $\text{R}_\text{F}\text{I}$ to produce the 1:1 adducts in good yields. The reaction of α -chloro- ω -iodoperfluoroalkanes with alkenes in the presence of the $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{--HCO}_2\text{Na}$ system gives addition products at the expense of the C–I bond without involving the

Table 24. Reactions of $\text{R}_\text{F}\text{I}$ with alkenes $\text{RCH}=\text{CH}_2$ in the presence of $\text{Na}_2\text{S}_2\text{O}_8$ in MeCN– H_2O .³⁹⁸

R	Yield of $\text{RCHICH}_2\text{R}_\text{F}$ for different $\text{R}_\text{F}\text{I}$ (%)		
	$\text{Cl}(\text{CF}_2)_4\text{I}$	$\text{Cl}(\text{CF}_2)_6\text{I}$	$\text{CF}_3(\text{CF}_2)_5\text{I}$
Bu^n	81	84	81
CH_2OH	73	83	61
C_6H_{13}	85	83	83
C_8H_{17}	83	85	85
C_9H_{19}	85	87	88
$\text{C}_{10}\text{H}_{21}$	83	84	—
$\text{C}_{14}\text{H}_{29}$	78	—	—

Note. Reactions were carried out at 60 °C for 6–8 h.

C–Cl bond.^{415,416} The reaction of perfluoroalkyl iodides with α -phenylstyrene carried out under identical conditions gives the corresponding adduct.²²³

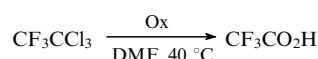


$\text{R}_\text{F} = \text{Cl}(\text{CF}_2)_4, \text{Cl}(\text{CF}_2)_6, \text{CF}_3(\text{CF}_2)_5$;

$\text{R} = \text{Bu}^n, \text{CH}_2\text{OH}, n\text{-C}_6\text{H}_{13}, n\text{-C}_8\text{H}_{17}, n\text{-C}_9\text{H}_{19}, n\text{-C}_{10}\text{H}_{21}, \text{Me}_3\text{Si}, \text{CH}_2\text{OCH}_2\text{CH}=\text{CH}_2$.

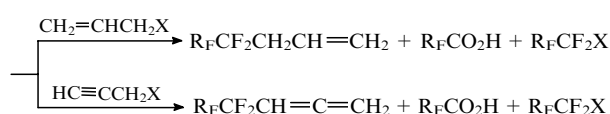
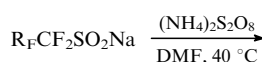
Reactions of sodium perfluoroalkanesulfonates $\text{R}_\text{F}\text{CF}_2\text{SO}_2\text{Na}$ with allyl halide and propargyl halide in the presence of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ result in good yields of 3-(perfluoroalkyl)prop-1-ene and 3-(perfluoroalkyl)allene, respectively.³²⁶

An interesting transformation of perfluoroalkyl iodides and -bromides as well as of compounds containing a CCl_3 group at the end of the perfluorinated carbon chain into the corresponding perfluorocarboxylic acids was observed in the presence of a redox system.^{132–144, 159, 193, 401, 417, 418}



Ox = $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{--HCO}_2\text{Na} \cdot 2\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{--oxalate}$, $\text{H}_2\text{O}_2\text{--FeSO}_4 \cdot 7\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{S}_2\text{O}_8\text{--Na}_2\text{S}_2\text{O}_4$, $\text{H}_2\text{O}_2\text{--Na}_2\text{S}_2\text{O}_4$, $\text{KBrO}_3\text{--Na}_2\text{S}_2\text{O}_4$, $(\text{PhCO})_2\text{O}_2\text{--PhNMe}_2$.

$\text{CF}_3\text{CCl}=\text{CHCH}_2\text{Cl}$ is the reaction product of CF_3CCl_3 with ethylene in the presence of Cr_2O_3 .⁴¹⁹ Perfluoroalkylation by perfluoroalkyl iodides and sodium perfluoroalkanesulfonates was performed using a variety of redox reagents and systems, *e.g.*, $\text{Ce}(\text{SO}_4)_2$, $\text{H}_2\text{O}_2\text{--FeSO}_4$, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, $\text{Pb}(\text{OAc})_4\text{--HOAc--Ac}_2\text{O}$, $\text{Mn}(\text{OAc})_3 \cdot \text{H}_2\text{O}$, *etc.* This reaction occurs *via* the intermediate formation of the perfluoroalkyl radical, since the introduction of compounds containing labile (C–Hal) bonds yields products of substitution of the $\text{R}_\text{F}\text{CF}_2$ group for the halogen atom.⁴²⁰



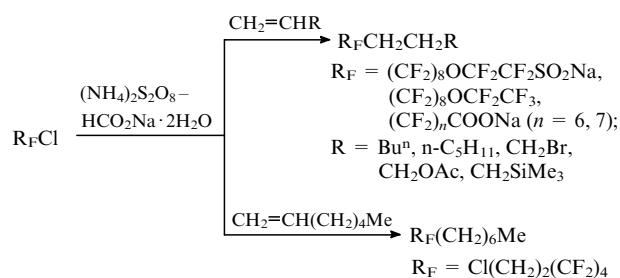
$\text{X} = \text{Cl}, \text{Br}$; $\text{R}_\text{F} = \text{Cl}(\text{CF}_2)_n$ ($n = 2, 4, 6$), $\text{CF}_3(\text{CF}_2)_n$ ($n = 3, 5, 7$).

The optimum conditions for this reaction are as follows: temperature below 40 °C and DMF as a solvent.

The use of redox systems allows for selective transformation of perfluoroalkyl iodides, α, ω -diiodoperfluoroalkanes and com-

Substrate	$T / ^\circ\text{C}$	t / h	Acid	Conversion (%)	Yield (%)
C ₆ F ₁₃ I	55	12	C ₅ F ₁₁ CO ₂ H	75	83.9
Cl(CF ₂) ₄ I	50	14	Cl(CF ₂) ₃ CO ₂ H	69	78.7
Cl(CF ₂) ₆ I	50	14	Cl(CF ₂) ₅ CO ₂ H	70	81.2
I(CF ₂) ₆ I	50	12	(CF ₂) ₄ (CO ₂ H) ₂	50	92.0
I(CF ₂) ₈ I	50	12	(CF ₂) ₆ (CO ₂ H) ₂	62	89.0
CF ₃ CCl ₃	25	10	CF ₃ CO ₂ H	100	72.5
CF ₃ CBr ₂ Cl	50	4	CF ₃ CO ₂ H	100	71.8
CCl ₃ CF ₂ CFCIBr	30	5	CF ₂ (CO ₂ H) ₂	100	74.6
CF ₂ (CCl ₃) ₂	30	5	CF ₂ (CO ₂ H) ₂	100	69.8
CF ₂ ClCFCl ₂	20	10	ClCF ₂ CO ₂ H	100	55.6
CF ₂ BrCFCIBr	15	20	BrCF ₂ CO ₂ H	100	63.4
CF ₂ ClCFCICF ₂ CFCl ₂	30	5	CF ₂ ClCFCICF ₂ CO ₂ H	100	78.6

System	Reaction conditions			Con- version (%)	Yield (%)
	solvent	$T/^{\circ}\text{C}$	t/h		
$(\text{NH}_4)_2\text{S}_2\text{O}_8 - \text{HCO}_2\text{Na}$	DMF	25	10	100	95
$\text{H}_2\text{O}_2 - \text{FeSO}_4$	DMF-H ₂ O	40	0.5	100	100
$(\text{NH}_4)_2\text{S}_2\text{O}_8 - \text{Na}_2\text{S}_2\text{O}_4$	DMF-H ₂ O	35	5	100	100
$\text{H}_2\text{O}_2 - \text{Na}_2\text{S}_2\text{O}_4$	DMF-H ₂ O	40	1	100	100
$\text{KBrO}_3 - \text{Na}_2\text{S}_2\text{O}_4$	DMF-H ₂ O	45	3	85	100
$(\text{PhCO}_2)_2 - \text{PhNMe}_2$	DMF	30	16	25	100



The intermediate perfluoroalkyl radical not only reacts with alkenes, but can undergo other transformations depending on the reaction conditions and the oxidant type. For example, reactions of sodium chloropolyfluoroalkanesulfonates yield dimerisation products, carboxylic acids and adducts to the multiple bond.³⁹⁶

Perfluoroalkylated alkenes are the main products in the reaction of sodium perfluoroalkanesulfonates with conjugated dienes in the presence of $\text{M}_2\text{S}_2\text{O}_8$.^{159, 427, 428}

The nature of other functional groups in the molecule can influence the lability of the C—Cl bond. For example, the activity of compounds of the type $\text{Cl}(\text{CF}_2)_7\text{X}$ ($\text{X} = \text{CO}_2\text{Na}$, CO_2Me , CO_2H) in the reaction with hept-1-ene decreases in the following order: $\text{Cl}(\text{CF}_2)_7\text{CO}_2\text{Na} > \text{Cl}(\text{CF}_2)_7\text{CO}_2\text{Me} > \text{Cl}(\text{CF}_2)_7\text{CO}_2\text{H}$.

In polyhalogenopolyfluoroalkanes containing I and Cl atoms, the latter is much less active than iodine. The chlorine atom reacts with hept-1-ene only after substitution of the SO_3Na group for iodine.

The perfluoroalkylation reaction can occur with different redox reagents and systems, *e.g.*, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$, H_2O_2 — FeSO_4 , $\text{Ce}(\text{SO}_4)_2$, $\text{Pb}(\text{OAc})_4$ — HOAc — Ac_2O , $\text{Mn}(\text{OAc})_3 \cdot \text{H}_2\text{O}$, *etc.* This reaction proceeds through the generation of the perfluoroalkyl radical and results in the products of substitution of the $\text{R}_\text{F}\text{CF}_2$ group for the halogen atom (Table 27).^{325, 326}

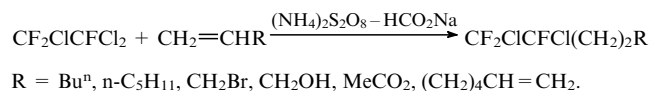


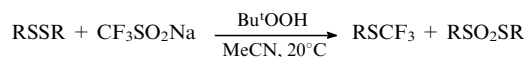
Table 27. Synthesis of 3-(perfluoroalkyl)prop-1-enes and 3-(perfluoroalkyl)allenes.³²⁶

Substrate	$\text{R}_\text{F}\text{CF}_2\text{X}$	Yield (%)	
		A	B
$\text{CH}_2=\text{CHCH}_2\text{X}$	$\text{Cl}(\text{CF}_2)_8\text{CF}_2\text{CF}_2\text{Br}$	75	10
	$\text{Cl}(\text{CF}_2)_8\text{OCF}_2\text{CF}_2\text{Cl}$	34	16
	$\text{CF}_3\text{CCl}_2\text{Br}$	46	33
	$\text{Cl}(\text{CF}_2)_2\text{Br}$	53	14
	$\text{Cl}(\text{CF}_2)_4\text{Br}$	62	10
	$\text{Cl}(\text{CF}_2)_6\text{Br}$	65	18
	$\text{Cl}(\text{CF}_2)_4\text{Cl}$	28	15
	$\text{Cl}(\text{CF}_2)_6\text{Cl}$	40	16
	$\text{CF}_3(\text{CF}_2)_3\text{Br}$	72	10
	$\text{CF}_3(\text{CF}_2)_5\text{Br}$	67	12
	$\text{CF}_3(\text{CF}_2)_7\text{Br}$	74	15
	$\text{CF}_3(\text{CF}_2)_7\text{Cl}$	32	17
$\text{HC}\equiv\text{CCH}_2\text{X}$	$\text{Cl}(\text{CF}_2)_2\text{Br}$	32	12
	$\text{Cl}(\text{CF}_2)_4\text{Br}$	46	20
	$\text{Cl}(\text{CF}_2)_4\text{Cl}$	27	30
	$\text{Cl}(\text{CF}_2)_6\text{Br}$	47	15
	$\text{CF}_3(\text{CF}_2)_3\text{Br}$	42	10
	$\text{CF}_3(\text{CF}_2)_5\text{Br}$	54	17
	$\text{CF}_3(\text{CF}_2)_7\text{Br}$	50	25

Note: A is $\text{R}_\text{F}\text{CF}_2\text{CH}=\text{CH}_2$, B is $\text{R}_\text{F}\text{CF}_2\text{CH}=\text{C}=\text{CH}_2$.

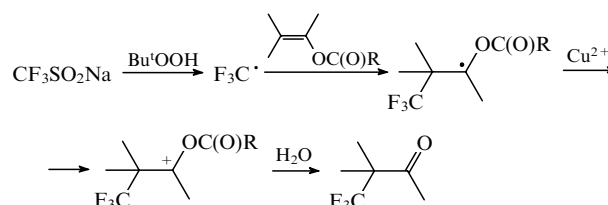
The reaction of perfluoroalkyl iodides with alkenes in the presence of H_2O_2 in acetone, MeCN or EtOH gives an addition product to the multiple bond in high yield.⁴⁰³

The reagent $\text{R}_\text{F}(\text{CF}_2)_n\text{SO}_2\text{Na} - \text{MoO}_2(\text{acac})_2$ is effective in perfluoroalkylation, *e.g.*, of disulfides, which occurs in the presence of $\text{M}_2\text{S}_2\text{O}_8$ ($\text{M} = \text{K}$, Na , NH_4) or Bu^tOOH in a mixture of water and a polar aprotic solvent, such as MeCN, DMF, dimethylacetamide, sulfolan, glymes, HMPT, *etc.*^{429–431}

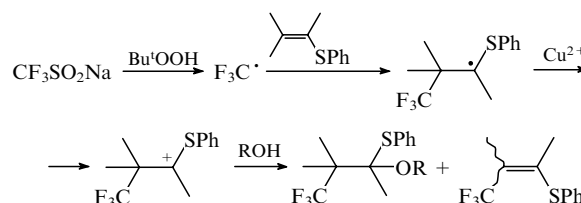


R	Yield of RSCF_3 (%)
$\text{Me}(\text{CH}_2)_6\text{CH}_2$	95
$(\text{CH}_2)_2\text{CO}_2\text{Et}$	75
$(\text{CH}_2)_2\text{CO}_2\text{Et}$	100
$\text{CH}_2\text{CO}_2\text{Et}$	60
$\text{CH}_2\text{CH}(\text{NH}_3^+)\text{CO}_2\text{Me}$	47
$(\text{CH}_2)_2\text{CH}(\text{NH}_3)\text{CO}_2\text{Me}$	55

Trifluoroalkylation of vinyl esters in the presence of Bu^tOOH results in α -trifluoromethyl ketones.⁴³²



Trifluoromethyl derivatives are formed in reactions of $\text{CF}_3\text{SO}_2\text{Na}$ with vinyl sulfides. The sulfur atom effectively stabilises the carbocation, which can be trapped by the reaction with a nucleophile, particularly, with an alcohol. α -Trifluoromethyl thioketals are the end products in this reaction.

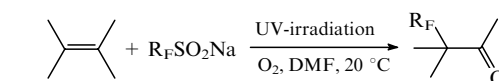


Aromatic compounds also undergo perfluoroalkylation in the presence of Bu^tOOH .⁴³³

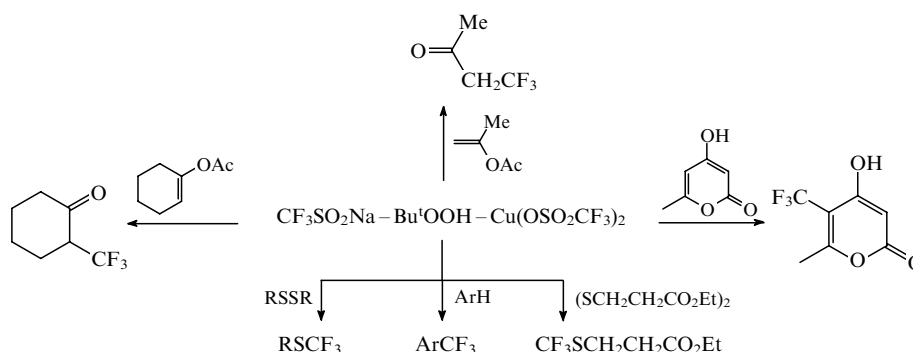
The trifluoromethyl radical can also be generated in the oxidation of the sodium trifluoromethanesulfinate by aqueous *tert*-butyl hydroxypoxide in the presence of Cu^{2+} (Refs 326, 432) and $\text{M}_2\text{S}_2\text{O}_8$ ($\text{M} = \text{K}$, Na , NH_4).^{430, 432–435} Some of these reactions are depicted in Scheme 2.

The $\text{CF}_3\text{SO}_2\text{Na} - \text{Bu}^t\text{OOH} - \text{Cu}^{2+}$ system can be used as a formal 'cationoid' reagent in the trifluoromethylation of arenes (Table 28).^{250, 253, 430, 432}

Perfluoroalkanesulfonates react with mono- and disubstituted alkenes in air or in oxygen with UV irradiation resulting in α -perfluoroalkyl ketones.²⁵³

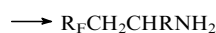
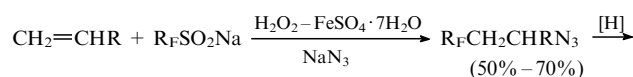


$\text{R}_\text{F} = \text{X}(\text{CF}_2)_n$, $n = 4, 6, 8$; $\text{X} = \text{F}$, Cl .



Scheme 2

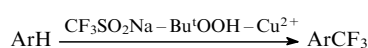
The reactions of terminal alkenes with sodium perfluoroalkanesulfonates in the presence of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ or the Fenton reagent ($\text{H}_2\text{O}_2 - \text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) proceed rather vigorously. In the presence of additional nucleophiles, side reactions of the intermediate carbocations are possible, which has been used for the synthesis of secondary amines.⁴³⁶

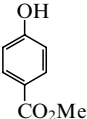
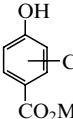
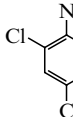

$$R_F = Cl(CF_2)_n (n = 4, 6), CF_3(CF_2)_5; R = Bu^n, n-C_7H_{15}, n-C_8H_{17},$$

$$AcO, CH_3OAc, (CH_2)_8CO_2Et.$$

Pyrrole and its derivatives undergo perfluoroalkylation under the action of perfluoroalkyl iodides in the presence of the $\text{H}_2\text{O}_2 - \text{FeSO}_4$ system in DMSO (Table 29).⁴³⁷

Table 28. Synthesis of trifluoromethylarenes.²⁵³



Substrate	Product	Yield (%)
PhOH		45 ^a
		21
		20
PhNH ₂		13
PhNHAc		52 ^b

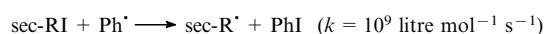
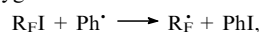
^aThe ratio of *ortho*:*meta*:*para* isomers is 4:1:6. ^bThe ratio of *ortho*:*meta*:*para* isomers is 4:1:2.

Table 29. Homolytic perfluoroalkylation of pyrrole by perfluoroalkyl iodides in the presence of hydrogen peroxide and FeSO_4 .⁴³⁷

Substrate	R _F I	Product	Yield (%)
	I(CF ₂) ₃ CF ₃		78
	I(CF ₂) ₃ CF ₃		55
	ICF(CF ₃) ₂		73
	I(CF ₂) ₂ CF ₃		64
	I(CF ₂) ₃ CF ₃		71
	I(CF ₂) ₃ CF ₃		73
	I(CF ₂) ₂ CF ₃		36
	I(CF ₂) ₂ CF ₃		30

3. Activation of perfluoroalkyl iodides by radicals

The above data suggest that under different reaction conditions perfluoroalkyl iodides can generate perfluoroalkyl radicals which further react with alkenes and aromatic compounds by a free-radical mechanism. Bravo *et al.*⁴³⁸ found that the radical Ph $\cdot$ can rapidly detach the iodine atom from secondary perfluoroalkyl iodides. This can be explained by the fact that the Ph—I bond is stronger than the R_F—I bond. The kinetics of the reaction of perfluoroalkyl iodides with the phenyl radical was studied by Kryger *et al.*⁴³⁹

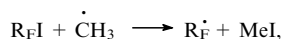


sec-R is secondary alkyl.

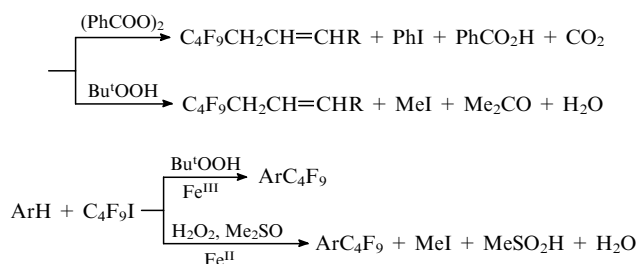
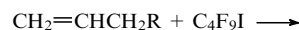
In other words, it is the iodide ion that is responsible for the electron transfer. It was thus suggested that perfluoroalkyl iodides can be activated by radicals generated from other substrates. For example, the methyl radical can activate the C–I bond.

In turn, the methyl radical is formed in the reaction of acetone or DMSO with hydrogen peroxide in trifluoroacetic acid or in the presence of Fe^{2+} salts, respectively. The methyl radical reacts with perfluoroalkyl iodide to produce a perfluoroalkyl radical. The

latter initiates further perfluoroalkylation of unsaturated or aromatic compounds.



Perfluoroalkyl radicals were generated by the following systems: $Bu^tOOH - Fe(OAc)_2OH$, $Me_2CO - H_2O_2$, $Me_2SO - H_2O_2 - Fe^{2+}$.⁴⁴⁰ These systems effect smooth perfluoroalkylation of aromatic compounds and alkenes (e.g., oct-1-ene, cyclohexene).



The ratio of isomers formed in perfluoroalkylation of aromatic compounds and the relative rates of these reactions suggest the radical mechanism of this reaction.⁴³⁸

Reductive perfluoroalkylation of alkenes with perfluoroalkyl iodides can be carried out in the presence of *tert*-butyl hydroperoxide in acetic acid (Table 30).⁴⁴¹

Table 30. Reductive perfluoroalkylation of alkenes by perfluoroalkyl iodides $R_F I$ in the presence of Bu^tOOH .⁴⁴¹

Alkene	R_F	Yield (%)
Hex-1-ene	C_4F_9	77
	C_8F_{17}	72
Oct-1-ene	C_4F_9	73
	C_8F_{17}	71
3,3-Dimethylbut-1-ene	C_4F_9	83
	C_8F_{17}	86
Cyclohexene	C_4F_9	85
	C_8F_{17}	73

It should be noted that this approach was first used in reactions of some aromatic compounds with perfluoroalkyl iodides and equimolar amounts of the peroxide.⁴⁴² It may be expected that after optimal conditions for such reactions are found, their role in perfluoroalkylation will increase.

IV. Conclusion

The data presented above testify to the increasing interest of investigators in the development of new approaches to the introduction of perfluorinated fragments into organic molecules and the transformation of simple substituents into complex functional groups. The novel perfluoroalkylating reagents considered above can be regarded as an alternative to classical and popular reagents. In particular, perfluoroalkyl iodides are widely used in perfluorination of unsaturated and aromatic organic substrates in the presence of initiators and catalysts. Radical perfluoroalkylation, syntheses of perfluoroalkanesulfinic and perfluorocarboxylic acids and polyfluorinated aldehydes as well as electrochemical synthesis of perfluoroalkyl derivatives offer obvious advantages because of simplicity and possibility to be used on an industrial scale. It remains to be hoped that further investigations will culminate in the discovery of other approaches to the synthesis of fluorine-containing compounds.

In this review, we made an attempt to demonstrate the most recent approaches and synthetic potentialities of novel reagents and to outline the main trends in the synthesis of perfluoroorganic compounds containing various molecular backbones and functional groups. This form of presentation of the experimental material makes it possible to contemplate the problem from the unusual for traditional chemistry standpoint and to propose certain original solutions based on the use of novel approaches to the generation of perfluoroalkyl radicals and their involvement in reactions with various compounds.

Needless to say, the practical implementation of the above-mentioned ideas and processes occurring by a single-electron transfer mechanism presents special interest not only for practitioners in fluoroorganic chemistry but also for specialists in organic synthesis and investigators elaborating radically new approaches to directed synthesis of organic molecules with the ultimate goal to develop new technologies. It should be noted that perfluoroorganic compounds often represent convenient, even unique models for the formulation and solution of fundamental problems of theoretical organic chemistry. In this context, the role of perfluorinated organic materials is steadily increasing, although the number of perfluoroalkylating agents which are suitable for large-scale production is still too small. A breakthrough in this area can be expected in the nearest future. The advent of advanced methodologies for transformation of organic compounds into valuable fluorine-containing products will speed up further progress in organic synthesis.

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Structure and properties of polymers in terms of the fractal approach

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Abstract. The review considers various manifestations of fractality in the description of the synthesis of macromolecules and the formation of the quasi-equilibrium state in polymers, fluctuation free volume, macromolecular frameworks, order parameters, and dissipative structures, acting as centres of shear stress in clusters. The possibility of numerical modelling of the properties of network polymers within the framework of fractal formalism is demonstrated. The methods for determination of the fractal dimension are described. The bibliography includes 248 references.

I. Introduction

The use in investigations of only Euclidean geometry, which describes objects with integer dimensions, restricts the possibility of adequate description of real (both natural and artificial) objects because it leaves numerous objects with fractional (fractal) dimensions beyond the scope of consideration. The properties of such objects can be described using fractal geometry.^{1,2}

Frequently encountered natural and synthetic polymers belong to the class of fractal objects. A polymer consists of long-chain macromolecules. Owing to this structure, polymers possess properties differing from those of other classes of solids. The most important parameters characterising a macromolecular chain are length and rigidity.^{3–5}

The structure of a vitreous polymer is thermodynamically unstable. Thermodynamically nonequilibrium processes result in the formation of fractal structures.⁶ A classical example supporting this statement is a fractured surface of a polymer. It has been found experimentally that the fractal properties of a fractured surface do not depend on the thermodynamic state of the solid.⁷ This is due to the thermodynamically nonequilibrium character of the fracture process.⁸ In the syntheses of polymers in solution (which is the most widely used variant⁹) the main structural unit is a macromolecular coil, which is known¹⁰ to be a fractal. To describe an object in terms of Euclidean geometry, only one

parameter, namely, the Euclidean dimension d , is needed, whereas description of fractal objects requires at least three parameters: the dimension d and the Hausdorff and spectral (fracton, d_s) dimensions.¹¹ Thus, the question of whether or not the methods of fractal analysis should be used to describe the structure of a macromolecular coil and a polymer is not a matter of researcher's choice but is dictated by the requirements of correct approach to the problem.[†]

The methods of fractal analysis and the models of irreversible aggregation provide a new understanding of the processes of synthesis and provide results which are difficult to obtain (or cannot be obtained) by other methods. All the foregoing has stipulated the scope of this review the purpose of which is to summarise the results of the use of fractal approach to the synthesis and analysis of the structures and properties of vitreous polymers.

II. Fractal analysis of the polymer structure

1. A model and the structure of a macromolecular coil

In order to develop a physically substantiated description for processes such as flocculation, polymerisation, *etc.*, various irreversible aggregation models, based on the physical pattern of formation of larger objects from smaller ones, have been developed.^{15–18} The necessity of using models of this type in this review is due to the fact that the processes they describe result in the formation of fractal objects.

The fractal dimension of a macromolecular coil in solution (D) is determined by two types of interaction: interactions of the coil elements with one another and solvent–polymer interactions.¹⁹ These types of interaction have been considered in detail.²⁰ In particular, the D value was found to depend on the chain rigidity, characterised by the Kuhn segment length (A). Linear $D(A)$ dependences have been found for flexible-, semirigid- and rigid-chain polymers (Fig. 1). An increase in the chain rigidity (an increase in A) is accompanied by a decrease in D ; this implies transition to less compact macromolecular coils.^{10,21} The D values obtained by extrapolation to $A = 0$ are different. The lowest value is obtained for rigid-chain polymers, which reflects the difficulty of formation of macromolecular coils in this case.²²

For flexible- and semirigid-chain polymers, the $D(A)$ plot at $A = 0$ extrapolates to $D = 2$, which corresponds to the dimension of the coil in a Θ -solvent.²⁰ Thus, only a hypothetical absolutely

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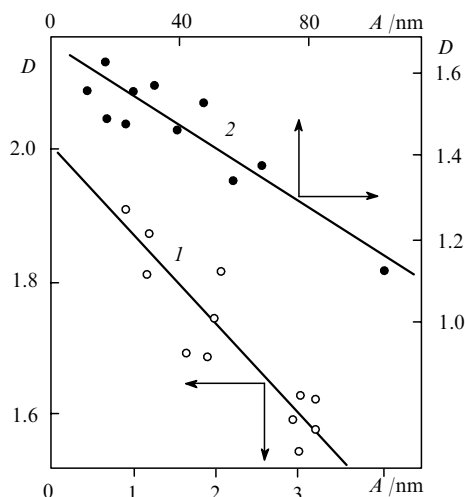


Figure 1. Fractal dimension D of a macromolecular coil vs. length of the Kuhn segment A for flexible- and semirigid-chain (correlation coefficient 0.82) (1) and rigid-chain polymers (correlation coefficient 0.85) (2).

flexible macromolecule ($A = 0$) can have an ideal conformation in a good solvent. In real polymer chains (for $A > 0$, i.e. actually, for an isolated macromolecular coil), this conformation can be attained by choosing a solvent which would counterbalance the effect of excluded volume.¹⁹ A similar extrapolation to $A = 0$ for rigid-chain polymers gives $D \approx 1.67$. This corresponds to the dimension of a coil in a good solvent.¹⁰ However, it should be noted that for these polymers, Θ -conditions can be created when the index in the Mark–Kuhn–Houwink equation $a \neq 0.5$ (or $D \neq 2$). For instance, Θ -conditions for polyarylate have been attained²² at $a = 0.8$, which is equivalent to $D \approx 1.67$ in conformity with the equation

$$D = \frac{3}{1+a} \quad (1)$$

Thus, different D values obtained for the above classes of polymers by extrapolation of the $D(A)$ plot to $A = 0$ can imply different criteria for the attainment of Θ -conditions.

Two alternative analytical expressions have been reported^{20,23} for evaluation of D as a function of the molecular characteristics of a polymer, C_∞ and S (C_∞ is the characteristic ratio, which is a measure of the statistical chain flexibility²⁴ and S is the cross-section area of the macromolecule)

$$C_\infty = \frac{D}{3(2-D)} + \frac{4}{3}, \quad (2)$$

$$D = 2 - 4 \left(\frac{2}{C_\infty S} \right)^{1/2}. \quad (3)$$

The D values determined from Eqns (2) and (3) were found to be in good agreement with those determined using Eqn (1).²⁰

The polymer–solvent interactions, which also influence the D value of a macromolecular coil in solution, can be characterised in several ways. One way is to use the Huggins constant k_H , which reflects the extent of polymer–solvent interaction.²⁴ The equation derived in terms of this approach shows the variation of D as a function of molecular mass M of the polymer²²

$$D = \frac{3 \ln M}{\ln M + \ln(7.14 k_H - 1) - \ln k_\eta - \ln k_H}, \quad (4)$$

where k_η is the constant in the Mark–Kuhn–Houwink equation.

The $D(k_H^{-2})$ dependence obtained experimentally²⁰ shows that both an increase in the rigidity and improvement of the thermodynamic quality of the solvent with respect to the polymer result in

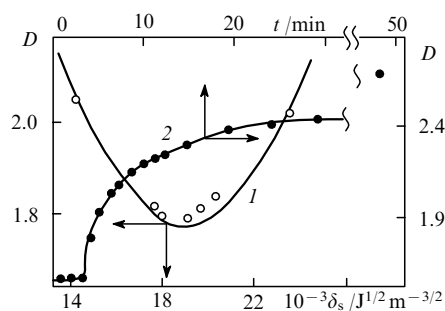


Figure 2. Fractal dimension D of a macromolecular coil for polyarylate vs. solubility parameter δ_s of the solvent used in the synthesis (1) and vs. reaction time t (2).

higher k_H . This in turn, decreases both k_H^{-2} and D . The correlation limits of $D(k_H^{-2})$ correspond to the range $1.5 < D < 2.286$; hence, this correlation can be used for predicting the structure of a macromolecular coil in dilute solutions.

Yet another parameter used to characterise the polymer–solvent interaction is the difference between the solubility parameters of the polymer and the solvent.²⁵ The plot for the variation of D of polyarylate vs. the solubility parameter of the solvent used in the synthesis of the polymer has a dome-like shape, typical of this type of dependence (Fig. 2, curve 1); this confirms the increase in D (an increase in the compactness of the macromolecular coil) following deterioration of the thermodynamic quality of the solvent.

The fractal dimension of a macromolecular coil D can serve simultaneously as a measure of volume interactions of this coil: for a coil in a Θ -solvent, D equal to 2 implies the absence of these interactions (the interaction parameter $\epsilon = 0$), $D < 2$ corresponds to repulsive interactions ($\epsilon > 0$), and $D > 2$ means attractive interactions ($\epsilon < 0$). A simple procedure for the determination of D is based on the equation²⁶

$$D = \left(\frac{5[\eta]}{[\eta]_\Theta^{2/3}} - 3 \right) \left(\frac{3[\eta]}{[\eta]_\Theta^{2/3}} - 2 \right)^{-1}, \quad (5)$$

where $[\eta]$ and $[\eta]_\Theta$ are intrinsic viscosities of the polymer dissolved in an arbitrary solvent and in a Θ -solvent, respectively.

By virtue of fractal analysis, one can gain some useful information, in addition to the data on molecular hydrodynamics, from the same experimental data.²⁷ This statement is illustrated below by some examples.

The fractal dimension D characterises the degree of ‘openness’ of the fractal structure — the lower D , the more efficient the penetration of particles into a fractal cluster (the more ‘accessible’ is the cluster for a reaction).²⁸ This is expressed analytically as follows:²⁹

$$Q \propto t^{(3-D)/2}, \quad (6)$$

where Q is the degree of conversion of a polymer and t is the current reaction time.

Equation (6) is the main scaling relation used to describe polymerisation kinetics.^{30–37} It is noteworthy that the process cannot take place for Euclidean coils (compact globules) because for them, $D = d = 3$ and $Q = \text{const}$. It is clear that in the general case, Eqn (6) should also contain diffusion parameters and the initial reactant concentrations.

An aspect related directly to the problem of macromolecular coil structure considered here is the dependence of aggregation processes on the concentration of aggregating particles c (initial concentration c_0) in some space.³⁸ If the density ρ of a cluster (macromolecular coil) decreases during the growth down to the density of the surrounding medium (the polymer–monomer solution), one type of universality of diffusion-limited aggregation

(DLA) is replaced by another type, namely, the particle–cluster aggregation switches to aggregation according to the Eden model;³⁹ subsequently, growth of the macromolecular coil ceases, having reached the critical radius R_c .³⁷ This variation of ρ is possible only for fractals because their density depends on the radius of gyration R_g , which is the critical radius for them³⁷

$$\rho \propto b R_g^{D-d}, \quad (7)$$

where b is a proportionality factor.

In the case of Euclidean objects, $D = d$ and $\rho = \text{const}$. The transition between the classes of universality considered in terms of the DLA model is preceded by yet another transition, namely, the cluster–cluster aggregation is replaced by the particle–cluster aggregation; this markedly decreases the rate of the reaction but does not stop it.⁴⁰

In terms of the cluster–cluster DLA, the synthesis of a polymer can be described using the relation^{40–42}

$$R_g \propto \left(\frac{4c_0 k T}{3\eta_0 m_0} t \right)^{1/D}, \quad (8)$$

where k is the Boltzmann constant, T is temperature, η_0 is the initial viscosity of the medium, t is the reaction time, and m_0 is the mass of a unit.

An increase in D implies an increase in the degree of branching of a macromolecular coil.²² This statement is illustrated by calculation of the spectral dimension d_s , which characterises the degree of connectivity of a fractal. The d_s value for a swollen fractal with allowance for the effect of excluded volume can be estimated from the following equation:⁴³

$$D = d_s \frac{d+2}{d-2}. \quad (9)$$

Note that for linear polymers, $d_s = 1$, while for branched polymers, $d_s = 1.33$.^{42, 43} The coil structure formed during the synthesis largely determines the molecular mass of the polymer formed. As D increases, the coil becomes more compact and the density of the coil diminishes.⁴⁴ The main models suitable in this case include the formation of a close packing of macromolecular coils, the appearance of an entanglement network, and the description of the self-acceleration effect with allowance for the concept of free volume. According to each of these models, the increase in the viscosity in the monomer–polymer system is the main reason for the formation of a macromolecular coil.⁴⁵

To describe the limiting regimes of the dynamics of the growth of aggregates in a reaction vessel with the initial monomer concentration c_0 , the characteristic length scale ξ was introduced,⁴⁶ which determines the qualitative transition from a fractal object to a non-fractal object

$$\xi \propto c_0^{-1/(d-D)}. \quad (10)$$

The former regime is realised for $R_g \ll \xi$, for a coil density much greater than the density of the medium in the reaction vessel and for the aggregate size (the degree of polymerisation for a macromolecular coil) N ; it can be written that⁴⁶

$$N(c_0, t) \propto (c_0 t)^{D/(2+D-d)}. \quad (11)$$

The latter regime is observed when $R_g \gg \xi$, the densities of the aggregate and the medium in the reaction vessel are nearly equal, and

$$N(c_0, t) \propto c_0^{(1+d)/(d-D)} t^d. \quad (12)$$

The relationship between N and Q in terms of the irreversible aggregation models can be elucidated using the main scaling relation (6) and relation (8), in which all the parameters, except for c_0 , η_0 and t , are assumed to be constant,

$$Q \propto c_0^{(D-1)/2} \eta_0^{(5-D)/2} N^{(3-D)/2}. \quad (13)$$

The resulting equation can be used to estimate the dependence of Q on t for the two regimes considered above. All these depend-

ences are non-linear and imply an increase in the reaction rate with an increase in t , that is, a self-acceleration effect.

A possible reason for self-acceleration is interpenetration of macromolecular coils compressed to the Θ -size with the formation of a stable network of molecular entanglements.^{47, 48} In some cases, under certain conditions of synthesis, in particular, for low c_0 and η_0 , the absence of self-acceleration is assumed.⁴⁵

It should be noted that the above variant for the calculation of $Q(t)$ does not take into account the exhaustion of the monomer during the reaction. Exhaustion of the monomer appreciably decreases the reaction rate. In other words, the effects of self-acceleration and exhaustion of the monomer act in the opposite directions. When c_0 values are low, the latter effect can suppress the former one.

An important process occurring during the synthesis of polymers is gelation; traditionally, it attracts considerable attention. However, there are several definitions of the gelation point and several methods for locating it on the $Q(t)$ curve. For example, the gelation point is found as the point in which the solution starts to exhibit some properties of a solid (elasticity, fragility, etc.).⁴⁸ In polymer syntheses, transition from the initial stage of polymerisation to the self-acceleration stage is referred to as gelation point.⁴⁹ The concept of gelation point used in polymer physics implies the point where the cluster which tightens the system (and extends from one system edge to the other) is formed.³⁶ Kolb and Herrmann⁵⁰ calculated the gelation point on the $Q(t)$ curve in terms of an approach based on the DLA models. Different approaches and different definitions of gelation cause uncertainty in its interpretation.

If the gelation effect is interpreted as the formation of a cluster tightening the system, the parameters describing this system change substantially.³⁶ Thus the velocity v of the migration of clusters (macromolecular coils) with mass m is assumed to be⁵⁰

$$v = m^\alpha, \quad (14)$$

where α is a scaling index.

At the point of gelation, the sign of α changes from negative to positive. This means that below the gelation point, smaller clusters are more mobile, whereas after the gelation point, the tightening cluster has the highest mobility.

Statistical geometric characteristics of the system also change in the gelation point. It has been shown both theoretically and experimentally³⁶ that D values of about 1.6–2.1, typical of a macromolecular coil in a solution, increase to ~ 2.5 (see Ref. 21), which is a value characterising a Witten–Sander cluster.¹⁵ In terms of the cluster–cluster DLA, the time dependence of R_g is written as⁵¹

$$R_g \propto t^{1/z}, \quad (15)$$

where the index z is related to D and α by the expression

$$z = D(1 - \alpha) - (d - 2). \quad (16)$$

Polymeric systems are often described using the size distribution function of clusters (macromolecular coils). In the physical chemistry of polymers, this function is defined as the molecular-mass distribution (MMD) function. The fractal dimension D provides little information on aggregation (polymerisation); this is a static value which does not describe the aggregation dynamics. In addition, D characterises the geometric properties of only one cluster (macromolecular coil) and cannot be used to describe sets of clusters in the system. For this purpose, one has to study the cluster size distribution function $n_s(t)$, where n_s is the number of clusters consisting of s units at time t .⁵²

The description of the cluster size distribution in the cluster–cluster DLA model has been analysed.^{40, 50, 52, 53} This model is completely suitable, for example, for the description of polymerisation of polymethyldiammonium chloride (PMDAC). The D value of this polymer, estimated to be 1.65 using Eqn (1), is a typical fractal dimension of aggregates formed during the clus-

ter-cluster DLA.³⁷ In view of this fact, the molecular mass distribution of PMDAC is described using the function⁵²

$$n_s(t) \propto s^{-2} t^z. \quad (17)$$

Let us consider methods used to estimate the parameters appearing in relation (17). The $n_s(t')$ values for the gelation point are found from the experimental MMD curves, $W_i(N)$, in the following way. It is assumed that $N = s$ and the part of the polymer corresponding to s_i is roughly equal to the total weight proportion of the polymer fraction W_i . By dividing W_i into s_i and by multiplying the ratio by the maximum degree of conversion Q_i , we obtain the $n_s(t')$ value. The index z is found from Eqn (16). In terms of the DLA model, the diffusion coefficient D_s is usually represented, by analogy with Eqn (14), in the form^{51,52}

$$D_s \propto s^\alpha. \quad (18)$$

In view of the definition of D_s (see Ref. 54), it can be easily found from Eqn (18) that

$$\alpha \propto -\ln \eta_0. \quad (19)$$

It was shown^{51,52} that α determines the pattern of the MMD function. For $\alpha < -0.5$, dome-shaped distribution curves having a maximum were obtained, and for $\alpha > -0.5$, the curves decay monotonically. The MMD curves for PMDAC are also dome-shaped. If we assume the equality sign in relation (19), α would vary from -1 to -3 , which completely complies with the experimental MMD curves. The position of the MMD maximum $N_{\max}$ is determined by the relation⁵⁵

$$N_{\max} \propto \frac{-\alpha}{1-\alpha}. \quad (20)$$

An increase in c_0 results in an increase in η_0 as well as in α and $N_{\max}$.

Figure 3 presents the variation of $\ln(s^2 n_s)$ vs. $\ln(st^z)$ for PMDAC samples synthesised at different c_0 . It can be seen that all experimental points fit in one curve. This is the most important result which confirms the legitimacy of using irreversible aggregation models for the description of polymerisation.

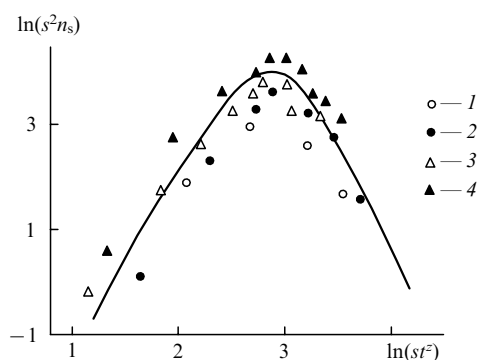


Figure 3. Generalised MMD curve as the function $\ln(s^2 n_s)$ vs. $\ln(st^z)$ for PMDAC synthesised at c_0 of 1.0 (1), 2.5 (2), 4.0 (3) and 5.0 (4) mol litre⁻¹.

The general curve shown in Fig. 3 can be used to predict the kinetics of MMD as a function of t . For this purpose, the $s = N$ value is first specified and the st^z value is determined for an arbitrary t . After that, the corresponding $s^2 n_s$ value is found using the plot in Fig. 3 and then W_i is calculated. The same calculation should be repeated for a different s , and so on.

The relationship between the structures of the macromolecular coil and a solid polymer and its influence on the glass transition temperature T_g have been analysed in relation to a series of vitreous amorphous copolymers — aromatic copolyestersulfon-formals (APESF). Transition to the condensed state implies a change in the environment of a macromolecular coil; the solvent

molecules surrounding the coil are replaced by similar coils. This changes the fractal dimension of the coil⁴⁴ and, correspondingly, the fractal dimension of the polymer structure as a whole.⁵⁶

To derive an analytical expression representing the relationship between the structure and properties of polymers, a definite quantitative model of the structure is required. The cluster model for the structure of the amorphous state of polymers was used for this purpose.⁵⁷ This model is based on the concept of local (short-range) order. The proportion of segments densely packed in the clusters φ_{cl} is a parameter of order, which is related to T_g by the following expression:⁵⁸

$$\varphi_{cl} \approx 0.03(T_g - T)^{0.55}, \quad (21)$$

where T is the testing temperature.

Within the framework of the cluster model, the glass-liquid transition is regarded as the thermofluctuational decomposition of clusters at $T = T_g$.⁵⁹ Fractal concepts are interrelated with the cluster model; the relationship between the main characteristics of these models is given in the form⁶⁰

$$d_f = d - 6 \left(\frac{\varphi_{cl}}{SC_\infty} \right)^{1/2}, \quad (22)$$

where d_f is the fractal dimension of the supermolecular (super-segmental) structure of the polymer

$$d_f = (d - 1)(1 + \mu), \quad (23)$$

where μ is the Poisson coefficient.

The S values for the sulfone and formal fragments which constitute APESF were assumed to be 35 and 23 Å², respectively,⁴⁸ and S values for copolymers were estimated using the condition of additivity. The C_∞ values were calculated from the equation⁶⁰

$$C_\infty = \frac{d_f}{d(d - d_f) + 4/3}. \quad (24)$$

Using Eqns (21)–(24), one can calculate T_g proceeding only from the structure of the macromolecular coil in solution, which is characterised by D , and from the molecular parameter S . The T_g values calculated by this procedure are in good agreement with experimental values; the discrepancy between them does not exceed 4% (Fig. 4).

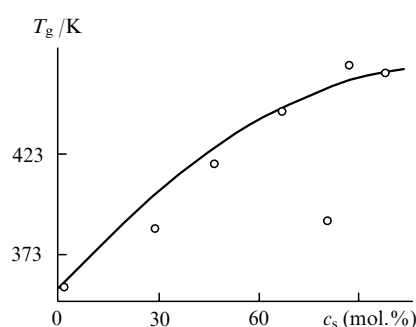


Figure 4. Glass transition temperature T_g vs. the content of sulfone fragment. The curve corresponds to experimental results and the points are calculated values.¹⁴

2. Hierarchy and evolution of dissipative structures in polymers

In recent years, principles of synergetics of nonequilibrium systems and fractal analysis have been used to study the relationship between the structures and properties of vitreous polymers,^{61–64} because an amorphous polymer is a thermodynamically nonequilibrium system.

The main feature distinguishing polymers from other classes of solids is that they consist of long-chain macromolecules. Therefore, it is natural to assume that the structural hierarchy of polymers (including network polymers) should be based on their molecular structure. In recent years, the characteristic ratio C_∞ has been used more and more frequently as a molecular parameter to describe the properties of polymers, instead of some other characteristics such as a/σ (a is the chain 'thickness' and σ is the chain rigidity).^{65,66} According to Boyer and Miller,⁶⁷ this is due to the fact that σ has greater uncertainty than C_∞ . Indeed, σ depends on the bond angles in the macromolecule, while C_∞ depends on the bond lengths, which are normally determined much more precisely than the bond angles. Without objecting to the legitimacy of this conclusion, we believe, nevertheless, that the reasons for the wide use of the parameter C_∞ are much more fundamental (see, for example, a number of studies^{60–64,68–71}). This can be demonstrated in relation to the epoxy polymers based on bisphenol A and cured by diamine (EP-1) and anhydride (EP-2). For example, to estimate the Bragg interval d_B for these polymers, wide-angle X-ray diffractometry has been used.⁷¹ The resulting value was used to determine the diameter ϕ (and, hence, the cross-section area S) of the molecule, simulated by a cylinder, from the following relation:

$$\phi \approx 1.22 d_B. \quad (25)$$

Subsequently, using the empirical relation⁷¹

$$T_g \approx 129 \left(\frac{S}{C_\infty} \right)^{1/2}, \quad (26)$$

where T_g is expressed in Kelvins and S is expressed in $\text{\AA}^2$, one can calculate the C_∞ values for epoxy polymers.

The behaviour of a solid subjected to mechanical treatment is determined by the processes of formation (disintegration) and evolution of dissipative structures (DS), which ensure the optimum mode of dissipation of the supplied energy.^{60,72,73} This general statement is valid for all polymers. Polymers have local order, which occurs as DS.^{74,75} However, direct application of the fundamental principles of thermodynamics and statistical physics of nonequilibrium systems to the investigation of the deformation of materials of a particular class is often difficult or even impossible without the knowledge of a definite quantitative model for the structure of this material. In the case of amorphous polymers, the cluster model is suitable for this purpose.^{57,74}

A specific feature of the DS formed in polymers is the existence of a universal hierarchy of space scales (structural levels), which is also reflected in the hierarchy of linear dimensions of the structure.^{60,63} Even elastically isotropic solids are characterised by at least three independent length scales, l_1 , l_2 and l_3 , which are related to one another⁷³

$$l_1 = a, \quad (27)$$

$$l_2 = aA_0, \quad (28)$$

$$l_3 = aA_0A_i, \quad (29)$$

where a is the minimum scale, A_0 and A_i are automodelling coefficients.

When choosing these length scales as applied to polymers, one should reject the atomic-size level because a polymer consists of long macromolecules. Therefore, the bond length in the macromolecular backbone l_0 , which is of the order of several angstroms, should be taken as the minimum scale a for polymers.^{62,76} Then the next (segmental) structural level would be determined by the length of statistical segment l_{st} , which is found from the equation

$$l_{st} = l_0 C_\infty.$$

Hence, provided that $l_1 = l_0$, it can be written for this structural level that^{77–79}

$$A_0 = C_\infty.$$

The next structural level for polymers is the topological level, the parameters of which are determined by characteristics of the network of macromolecular entanglements ('loops') in linear polymers or the network of chemical cross-links in cross-linked polymers. The characteristic length for this level is the distance between the entanglement points or chemical cross-linking points R_s

$$R_s = 18 \left(\frac{2V_{cl}}{F} \right)^{-1/3}, \quad (30)$$

where V_{cl} is the density of the cluster network of entanglements, F is the cluster functionality.

If the equality $A_0 = C_\infty$ is retained for the subsequent structural levels, Eqns (27)–(29) for polymers can be written in the form

$$l_1 = l_0, \quad (31)$$

$$l_2 = l_{st} = l_0 C_\infty, \quad (32)$$

$$l_3 = R_s = l_0 C_\infty^2. \quad (33)$$

Figure 5 shows the dependence of R_s vs C_∞^2 . Splitting of the plot into two straight lines is due, first, to the great scatter of the published data^{62,76,80} and, second, to different approaches to the interpretation of the $l_2 = l_{st}$ value.^{62,81} Nevertheless, the fact that R_s is proportional to C_∞^2 confirms that C_∞ is the automodelling coefficient for the transition of the scale of DS dimensions from l_{st} to R_s .

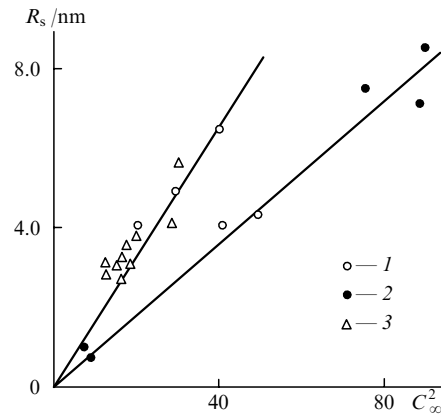


Figure 5. Distance between entanglements (chemical cross-linking points) vs. characteristic ratio for amorphous vitreous (1), amorphous-crystalline (2) and cross-linked (3) polymers.⁷⁹

Figure 6 illustrates the relationship between the R_s values calculated from Eqns (30) and (33). Aharoni⁷⁶ noted an increase in R_s following an increase in the chain flexibility (increase in C_∞) for a large number of linear polymers

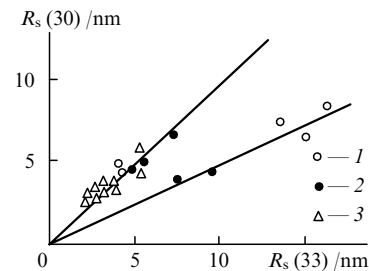


Figure 6. Relationship between the distances between entanglements (chemical cross-linking points) R_s calculated from Eqns (30) and (33) for amorphous glassy (1), amorphous-crystalline (2) and cross-linked (3) polymers.⁷⁹

$$R_s \approx 10 C_{\infty}. \quad (34)$$

A similar relation holds for cross-linked polymers

$$R_s \approx 5 C_{\infty}. \quad (35)$$

Thus, the C_{∞} value, which is correlated with R_s , appears to be controlled by the polymer topology, which can be varied by varying the cross-linking density v_s .

Polymers are characterised by one more, specific length scale; this is the section of a macromolecule between entanglement points or chemical cross-linking points L_s , which can be determined from the equation

$$L_s = \frac{F_{ch}}{2Sv_s}, \quad (36)$$

where F_{ch} is the functionality of a chemical cross-linking point ($F_{ch} = 4$).¹⁴

Figure 7 shows the variation of L_s vs. C_{∞}^3 , which can be approximated by a straight line passing through the origin of coordinates. The L_s/C_{∞}^3 ratio has the order of l_0 .^{62, 76} Hence, for this structural level, typical of polymers, C_{∞} can be accepted as the automodelling coefficient.^{82–84}

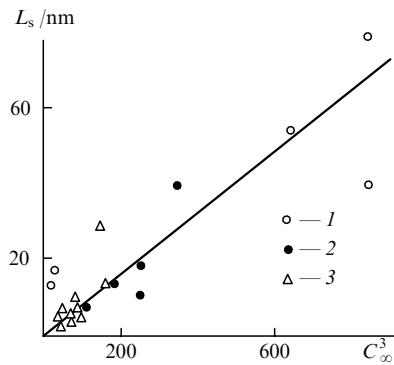


Figure 7. Length of the section of a macromolecule between entanglements (chemical cross-linking points) L_s vs. characteristic ratio C_{∞}^3 for amorphous glassy (1), amorphous-crystalline (2) and cross-linked (3) polymers.⁷⁹

Let us consider the evolution of DS in network polymers during deformation. It has been shown⁷⁴ that plastic yield in amorphous polymers occurs exactly in clusters, the yield point being dependent only on the density of the cluster network of entanglements (v_{en}), i.e. on the number of closely packed segments in unit volume of the polymer. Yield can be regarded as the loss of stability of clusters in the field of mechanical stress, while cold flow is the deformation of a devitrified loosely packed matrix in which the role of chemical cross-links is played by the cluster network of entanglements.⁸⁵ This interpretation permits one to specify the structural changes occurring during deformation of network polymers in terms of the percolation cluster model.^{60, 72–74}

As noted above, the DS formed (or existing) in a solid subjected to deformation are distinguished by a universal hierarchy of structural levels.⁸⁶ Balankin^{87, 88} suggested that the hierarchical structure of the DS in a solid is based on a fundamental feature, i.e. shear stability, which stipulates the difference between the characteristic space scales of the regions of localisation and dissipation of energy ‘pumped’ into the solid on external treatment. The characteristic scale of the regions (l_s) in which excess energy is dissipated is proportional to the shear modulus G . Since, in terms of the cluster model, these regions can be associated with clusters, it is expedient to use the characteristic size l_{st} as l_s . Figure 8 illustrates the relationship between G and l_{st} , which is approximated by a straight line that passes through the origin of coordinates. This confirms the legitimacy of using l_{st} as l_s .

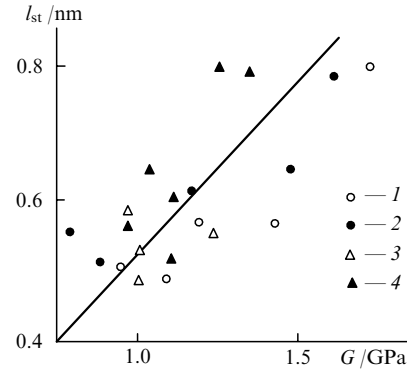


Figure 8. Relationship between the length of statistical segment l_{st} and the shear modulus G for EP-1 (1), EP-2 (2) and for EP-1 (3) and EP-2 (4) samples cured at a hydrostatic pressure of 200 MPa.⁷⁸

With allowance for the above interpretation of cold flow and for Eqn (30), the distance between the clusters R_{cl} should be accepted as the next level in the hierarchy of structural levels. The characteristic size of the regions of localisation of the ‘pumped-in’ energy is

$$l_e \propto B + \frac{4}{3}G, \quad (37)$$

where B is the bulk modulus.⁷³ The possibility of equating R_{cl} and l_e is verified in the following way. The ratio of the space scales of the DS of adjacent structural levels, L_i and L_{i+1} , is expressed as follows:⁷³

$$\frac{L_{i+1}}{L_i} = \frac{l_e}{l_s} = \left(B + \frac{4}{3}G \right) G^{-1} = A_i. \quad (38)$$

It is clear that the multiplication of the ratio $[B + (4/3)G]/G$ by l_s , which is equal to l_{st} , gives l_e . The R_{cl} value can be estimated using Eqn (30).

The dependence of l_e on $[B + (4/3)G]$ also proved to be linear (Fig. 9), which implies that the parameter l_e can, in principle, be used as the characteristic size of the regions of localisation of the pumped-in energy. However, this assumption can be ultimately confirmed by comparing l_e and R_{cl} . A correlation between these parameters has been found;⁶⁰ it was shown that R_{cl} regularly exceeds l_e by ~ 0.8 nm. This relationship between l_e and R_{cl} can be interpreted by virtue of the cluster structure model for an amorphous polymer (Fig. 10).⁸⁹ Evidently, the decrease in R_{cl} by ~ 0.8 nm, which is roughly equal to l_{st} , means that the pumped-in energy does not spread throughout the whole polymer bulk but is localised only in the loosely packed matrix because a cluster with the characteristic size l_{st} is excluded from consideration. Compar-

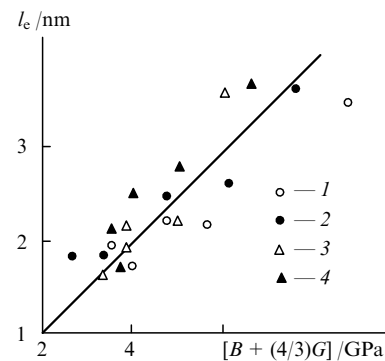


Figure 9. Relationship between the characteristic size of the regions of localisation of the pumped-in energy l_e and the parameter $[B + (4/3)G]$. For designations, see Fig. 8.⁷⁸

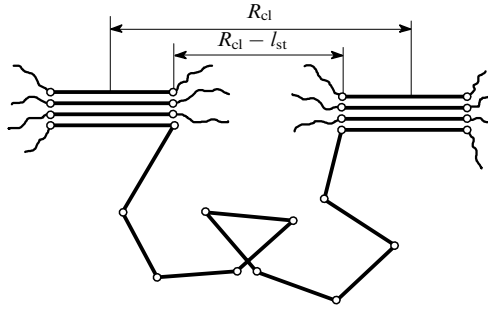


Figure 10. Parameters of the cluster structure model for an amorphous polymer.

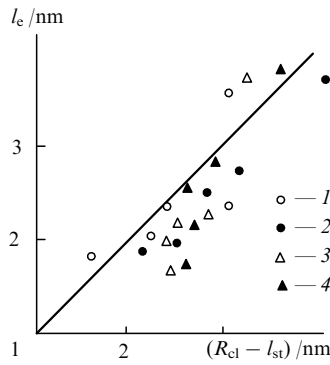


Figure 11. Relationship between the characteristic size of the regions of localisation of the pumped-in energy l_e and the $(R_{cl} - l_{st})$ value. For designations, see Fig. 8.

ison of the l_e value and the difference $R_{cl} - l_{st}$ (Fig. 11) confirms this conclusion. Hence, the structural characteristics l_e and $R_{cl} - l_{st}$, estimated within the framework of the cluster model and regarded as the space scales of the DS of adjacent levels [see Eqn (38)], allow one to estimate the automodelling coefficient for the mechanical deformation of a network polymer A_i , which is equal to the fractal dimension D_f of the regions of localisation of excess energy in a plastically deformed medium. In a first approximation, the D_f value can be expressed in terms of the Poisson coefficient μ in the following way:⁷²

$$D_f = 2 \frac{1 - \mu}{1 - 2\mu}. \quad (39)$$

The relationship between the dimension D_f and the automodelling coefficient A_i for the network polymers under consideration is illustrated in Fig. 12. It can be seen that both the magnitudes

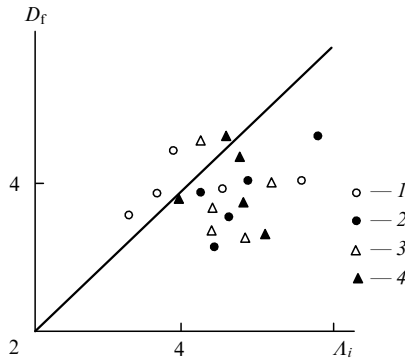


Figure 12. Relationship between the fractal dimension of the regions of localisation of excess energy D_f and the automodelling coefficient A_i . For designations, see Fig. 8.

and the patterns of variation for these parameters coincide. Thus, plastic yield and cold flow of network polymers are adequately described in terms of the thermodynamics of nonequilibrium processes and the cluster model of amorphous polymers provides a correct description of the structure of network polymers. It is also evident that clusters are identified as DS.

Similar results have been obtained for film samples of a linear polymer — polyarylatesulfone.⁹⁰ Using Eqn (38) and the ratio¹⁴

$$\frac{L_s}{l_{st}} = \left(\frac{R_s}{l_{st}} \right)^D, \quad (40)$$

it can be shown that

$$A_i = D_f \approx \left(\frac{L_s}{l_{st}} \right)^{1/D}. \quad (41)$$

Figure 13 shows that the L_s values estimated from Eqns (36) and (41) are in good agreement with each other. This implies that the sections of a macromolecule between entanglements and between clusters also obey (are controlled by) the DS hierarchy.⁹⁰

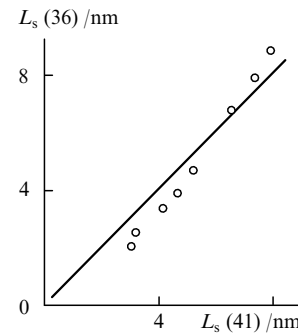


Figure 13. Relationship between the lengths of macromolecule sections between entanglements determined using Eqns (36) and (41) for polyarylatesulfone.⁹⁰

In view of the foregoing, it can be suggested that the automodelling coefficient A_i in Eqn (38) is equal to C_∞ . Then this equation assumes the form

$$\frac{B}{G} + \frac{4}{3} = C_\infty. \quad (42)$$

The B and G values can be expressed in terms of Young's modulus (E) and the fractal dimension of the polymer structure d_f in the following way:⁹¹

$$B = \frac{E}{d(d - d_f)}, \quad (43)$$

$$G = \frac{E(d - 1)}{2d_f}, \quad (44)$$

where $d = 3$.

Using Eqns (42)–(44), one can estimate quantitatively the relationship between the molecular parameter C_∞ and the fractal dimension d_f .⁹²

$$\frac{2d_f}{d(d - 1)(d - d_f)} + \frac{4}{3} = C_\infty. \quad (45)$$

The dependences of d_f found from Eqns (23) and (45) for various classes of polymers are presented in Fig. 14. It can be seen that the results are in good agreement with each other. It is noteworthy that the methods of calculation are completely independent — Eqn (23) employs the results of mechanical testing, while Eqn (45) is based on published data for C_∞ .⁹²

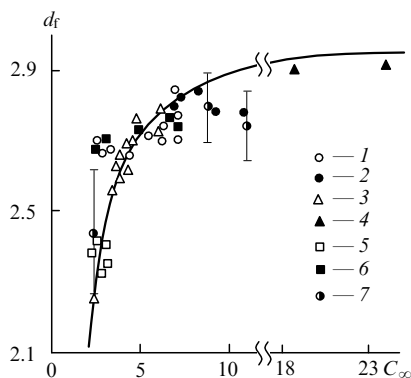


Figure 14. Fractal dimension of the structure d_f of polymers vs. characteristic ratio C_∞ .

Solid line — calculation from Eqn (45); dots — calculation from Eqn (23): (1) linear polymers, impact testing; (2) linear polymers, calculation of d_f from the data of Ref. 60; (3) cross-linked epoxy polymers; (4) super-high-molecular-mass polyethylene produced by solid-phase extrusion; (5) polyarylate prepared by solid-phase extrusion at $T > T_g$; (6) linear polymers, stretching testing; (7) linear polymers, calculation of d_f from small-angle X-ray diffraction data. For sample (7) experimental data on the inaccuracy are given.⁶⁰

The evolution of DS induced by various types of treatment of the polymer has been considered.^{64,93,94} Figure 15 shows the dependence of the cluster functionality F on the curing agent: oligomer ratio (K_{st}) for epoxy polymers in deformed and non-deformed states. The most characteristic distinction between the plots being compared is the substantial increase in F after the yield point. The simultaneous decrease in V_{cl} and increase in F upon deformation of polymers up to the yield point^{63,64} implies decomposition of unstable clusters characterised by relatively low F to leave only stable clusters with large F .⁹⁵ The decay of unstable clusters induces mechanical devitrification of the loosely packed matrix; this explains the plastic behaviour of the polymer in the plateau of forced rubber-like elasticity (cold flow).^{96,97}

The opposite situation is observed during heat ageing, namely, the local order (V_{cl}) increases and the molecular mobility of chains is suppressed (D decreases).⁹⁴

Experimental evidence for the fractality of the cluster structure (or DS) has been obtained using wide-angle X-ray diffraction analysis.^{98–100} The integral intensity of the amorphous halo I_{cl} can be regarded as a measure of distributed particles (clusters), while its half-width can be taken as a measure of their effective size; the relationship between these values is illustrated in Fig. 16

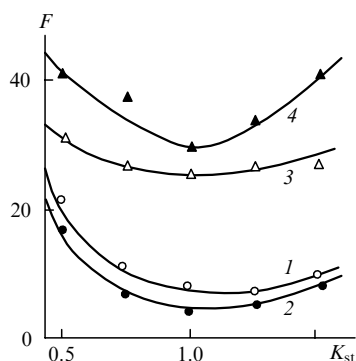


Figure 15. Functionality of clusters vs. the curing agent: oligomer ratio for epoxy polymers EP-1 (1, 3) and EP-2 (2, 4) before (1, 2) and after (3, 4) the yield point has been attained.

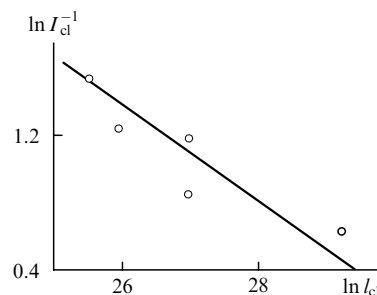


Figure 16. Reciprocal integral intensity of X-ray scattering vs. cluster half-width for EP-1.⁹⁸

in relation to EP-1. The $I_{cl}^{-1}(l_{cl})$ dependence presented in the logarithmic coordinates is readily transformed into the form⁹⁸

$$I_{cl}^{-1} \propto l_{cl}^{d_f}, \quad (46)$$

where $d_f \simeq 2.70$.

This type of dependence is typical of fractal structures; it can serve as experimental evidence confirming the fractality of the polymer structure. In addition, the d_f value is in good agreement with the fractal dimensions found for other epoxy polymers (see, for example, Ref. 69).

A fundamental description of the process of polymer fracture which includes the dilaton concept^{101–103} as a constituent has been proposed.¹⁰⁴ The dilaton model assumes the formation of a negative density fluctuation, dilaton, the length of which is determined by the free path of phonons Λ_f . In this case, the overload factor χ on the bonds being ruptured depends on Λ_f and on the interatomic distance a_{at} .¹⁰¹

$$\chi = \frac{\Lambda_f}{a_{at}}. \quad (47)$$

The Λ_f values found for oriented polymers are about 10 nm and χ are about 30–40.¹⁰³ However, for nonoriented polymers, it was found that $\chi \leq 1$, i.e. $\Lambda_f \leq a_{at}$. These dilatons were called ‘degenerate’ (practically, this means that phonons have no free path).^{105–107}

The use of the fracton concept²⁸ provided a fundamental interpretation for this seeming contradiction. Fractons are vibrational excitations localised on a fractal. Since the chain section between entanglements or cross-links is a fractal, a phonon localised on this section becomes a fracton. Localisation of a phonon means that it has no free path; this accounts for the fact that $\chi \leq 1$.

During orientation of a polymer, the chain section in question is stretched; finally, it becomes straight. In this case, its Hausdorff dimension is equal to the topological dimension

$$D = d_t = 1 \quad (48)$$

and the fractal behaviour switches to the Euclidean behaviour: the phonon becomes delocalised and acquires some free path controlled by the structure of the oriented polymer. Now $\chi > 1$. Thus, the dilaton concept is actually a specific case of the fracton theory (for $D = 1$).¹⁰⁴

The following relationship between the parameters χ and D has been obtained.¹⁰⁴

$$\chi \simeq D^{-2}. \quad (49)$$

An increase in the molecular mobility (increase in D) results in stress relaxation on the non-oriented polymer chains ($\chi < 1$).¹⁰⁸

Since characteristics of fractal analysis are general, the relationship between the structures of different aggregation (physical) states of the polymer can be established. For example, a macromolecular coil (cluster) in solution and the polymer structure in the condensed state are fractals with the dimensions D and d_f , respectively.^{44,109} This fact can be used to predict the structure of a solid polymer even at the stage of synthesis.^{110–112} The D value,

with allowance for the effect of excluded volume, is determined by Eqn (9). For linear polymers, it should be accepted that d_s in this equation is equal to 1.⁴³ Transition to the condensed state is accompanied by the change in the environment of a macromolecular coil; a coil becomes surrounded by similar coils instead of solvent molecules. This results in the change of the fractal dimension d_f for the condensed state⁴⁴

$$d_f = \frac{d_s(d+2)}{2}. \quad (50)$$

For linear polymers, provided that $d_s = 1$ and $d = 3$, it follows from Eqns (9) and (50) that¹¹¹

$$d_f = 1.5D. \quad (51)$$

Equation (51) clearly demonstrates the relationship between the coil structure in solution and the structure of the condensed polymer.

3. Quasi-equilibrium state of polymers

Neither completely ordered nor completely disordered polymers have been obtained to date. One reason for this situation is the chain nature of polymer molecules (in particular, the formation of loops during crystallisation).¹¹³ The tendency for transition to a more equilibrated state in polymers is often attributed to an increase in the degree of ordering.¹¹⁴ Therefore, it can be assumed that processes in which this tendency is manifested (for example, heat ageing, thermosetting, *etc.*) are subject to a competition of two opposing mechanisms. An increase in the degree of ordering is counteracted by the entropy of 'stretching' of macromolecules. When the thermodynamic forces of these mechanisms have been balanced, the polymer reaches some quasi-equilibrium state.⁶⁰ Perturbation of the balance in either direction governs the pattern of changes in the polymer structure. In other words, under certain conditions, a polymer can be transformed not only towards a more equilibrated state but also away from equilibrium. According to its physical essence, the latter process can be called 'antirelaxation'. Some causes and consequences of this process are considered below in terms of the cluster model of the structure of the amorphous state of polymers and cluster analysis.

Thermosetting of extruded specimens of polyarylate occurs in the loosely packed matrix;¹¹² therefore, the D_f value should be taken as the fractal dimension which determines the process in a structural element (for example, in a tube). Figure 17a shows the variation of the thermosetting ψ as a function of D_f for extrudates, which implies that the thermal shrinkage changes its sign when $D_f \approx 3$. This fact is very interesting by itself. In the case of extrudates with $D_f > 3$, a less closely packed structure (having greater D_f) is transformed during relaxation (thermosetting) into a more closely packed structure (having smaller D_f), which is, therefore, closer to equilibrium. The behaviour of specimens with $D_f < 3$ requires clarification. At the first glance, it seems that as D_f decreases and the structure changes, $\psi = 0$ should imply termination of thermosetting. However, this does not occur; instead, ψ only changes its sign. This effect can be easily explained

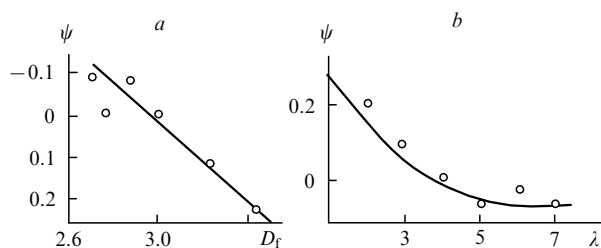


Figure 17. Thermosetting ψ vs. the dimension of the regions of localisation of excess energy D_f (a) and extrusion draw ratio λ (b) for polyarylate extrudates.

by two specific features of the cluster model — arbitrary orientation of the cluster axes in space and connection of clusters by 'interpenetrating' chains, which are subject to the limitations of the Gaussian statistics.⁹⁷ This means that it is impossible to attain a close packing of clusters, *i.e.* conditions of thermodynamic equilibrium cannot be reached in an amorphous polymer. This has been the reason for the introduction of the above-mentioned concept of 'quasi-equilibrium state',¹¹⁵ in which forces due to which a polymer tends to a thermodynamic equilibrium and, hence, to an increase in the degree of local ordering are counterbalanced by entropy forces of the 'interpenetrating chains'. The last-mentioned fact can induce transition of an amorphous polymer from a thermodynamically more equilibrated state to a less equilibrated state. Experimental dependence of ψ on the draw ratio λ confirms this direction of the thermosetting process (Fig. 17b).

The most characteristic feature of the relationship between D and d_f (Fig. 18) is the fact that the limiting value $D = 1$ is attained at $d_f = 2.5$ rather than at $d_f = 2$. Recalling that the dimension D characterises the mobility (deformability) of the section of a macromolecule between chemical cross-linking points (entanglement points) and $D = 1$ implies the loss of molecular mobility by this section. The quasi-equilibrium state corresponds to 'freezing' of the molecular mobility of polymer chains and, as a consequence, to the transition to brittle fracture, which is realised at $D_f < 3$.⁸⁷ Since D_f and d_f are related to each other as follows⁸⁷

$$D_f = 1 + \frac{1}{3 - d_f}, \quad (52)$$

it can be readily seen that $d_f = 2.5$ corresponds to $D_f = 3$.

When examining the dependence of d_f on the relative portion of the loosely packed matrix ϕ_{lp} in poly(methyl methacrylate), high-density polyethylene, polycarbonate, and polyarylate (Fig. 19), attention is drawn by the fact that for $\phi_{lp} = 0$ (the hypothetical state characterised by full local ordering), the d_f values are extrapolated to certain d_f^0 values (which are different for different polymers), exceeding the lower limiting value, equal to 2. Using published data for C_∞ (see, for example, Ref. 113), one can calculate the theoretical d_f^0 values from Eqn (45) and compare them with the limiting d_f^0 value (see Fig. 19). The parameters d_f^1 and d_f^0 are well correlated (Table 1), which reflects the occurrence of a quasi-equilibrium state. Using Eqn (45) and the relation

$$\phi_{cl} = C_\infty l_0 S V_{cl}, \quad (53)$$

the following limits can be identified: for $C_\infty > 3$, a quasi-equilibrium state cannot be attained at all; for $C_\infty = 2-3$, it may happen that $D_f < 3$; the value $d_f = 2$, corresponding to $D_f = 2$ is reachable only for a polymer with $C_\infty = 2$. Analysis of the results obtained in terms of Eqn (45) as well as the data given in Fig. 19 and in Table 1 show that Eqn (45) determines the minimum d_f values possible for a given C_∞ .

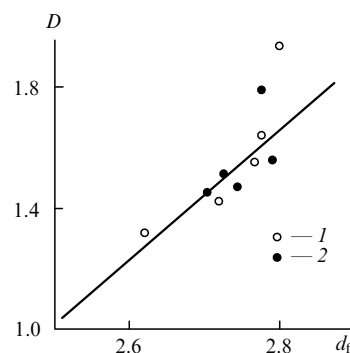


Figure 18. Relationship between the fractal dimensions of the macromolecule section between cross-linking points D and of the structure d_f for epoxy polymers EP-1 (1) and EP-2 (2).

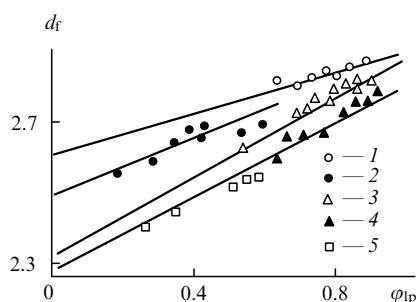


Figure 19. Fractal dimension of the structure d_f vs. proportion of the loosely packed matrix ϕ_{lp} for poly(methyl methacrylate) (1), high-density polyethylene (2), polycarbonate (3), polyarylate (4), and polyarylate extrudates (5).

Table 1. Fractal dimensions of the polymer structures d_f^1 and d_f^0 .

Polymer	d_f^1	d_f^0
Poly(methyl methacrylate)	2.55	2.60
High-density polyethylene	2.53	2.49
Polycarbonate	2.29	2.31
Polyarylate	2.23	2.27
Epoxy polymer	2.58	2.51

This accounts for the discrepancies between the d_f values found from relations (23) and (45) — the former gives the real d_f value and the latter gives the minimum possible one.

The dependences of D_f on the curing agent : oligomer ratio (Fig. 20) for EP-2 specimens immediately after the manufacture (curve 1) and after keeping at room temperature for 1.5 years (physical ageing) (curve 2) show that during ageing, D_f approaches 3, this effect being more pronounced for nonequilibrium systems with a deficiency or an excess of a curing agent. The minimum C_∞ value for the epoxy polymer with $K_{st} = 1.0$ is equal to 3.38.⁷¹ With allowance for this fact, an estimate of the minimum D_f value also gave ~ 3.38 . This estimate is in good agreement with the experimental D_f value for the aged polymer ($D_f \approx 3.16$).

The existence of the quasi-equilibrium state is also confirmed by the temperature dependences of the density fluctuations $\langle \Delta\rho/\rho \rangle^2$ (Fig. 21), which diminish as the temperature rises and tend to zero for $T = 0$, which corresponds to an ideal structure. However, there occurs a transition at temperature T^* below which $\langle \Delta\rho/\rho \rangle^2$ deviates from the predicted pattern¹¹⁶ and remains constant as the temperature varies. The density fluctuations above T^* are supposed to be due to the local mobility of the sequences in the polymer backbone but below T^* this mobility becomes ‘frozen’. This interpretation is fully consistent with the concept

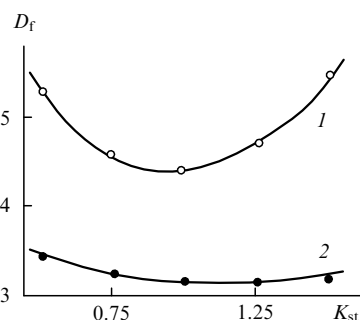


Figure 20. Dimensions of the regions of localisation of excess energy D_f vs. the curing agent : oligomer ratio K_{st} for EP-2 samples immediately after preparation (1) and after physical ageing (2).

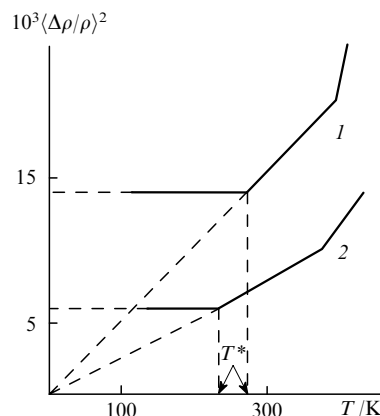


Figure 21. Temperature dependences of the density fluctuations $\langle \Delta\rho/\rho \rangle^2$ for poly(methyl methacrylate) (1) and poly(ethylene terephthalate) (2).¹¹⁷

of quasi-equilibrium state ($D = 1$). The nature of the temperature T^* has been considered in detail.¹¹⁷

Thus, the introduction of the concept of quasi-equilibrium state in polymers provides interpretation of some experimental facts. The application of the cluster model and fractal analysis makes it possible to specify the direction of the process of synthesis and to estimate its main characteristics.

4. Fluctuation free volume in polymers

The properties of polymers are mainly related to the molecular mobility and structure, which is determined by the degree of ordering of macromolecules.¹¹⁸ Free volume, or, more precisely, one of its components, fluctuation free volume, is one of the parameters most suitable for phenomenological description of a structure.¹¹⁹ As a rule, the fraction of the fluctuation free volume f_{iv} is estimated on the basis of polymer properties rather than from structure characteristics. Within the framework of the cluster model of the amorphous state of polymers,^{74, 120, 121} it has been shown⁵⁷ that a microcavity of fluctuation free volume is formed upon detachment (dissociation) of a segment from a region of local order (cluster) and ‘collapses’ upon attachment of a segment to a cluster. If this mechanism is accepted, at least two aspects need to be considered. One aspect concerns the energy characteristics of the process. The cluster model for the structure of the amorphous state of polymers postulates the thermofluctuational character of local ordering, according to which the number of segments in clusters diminishes as the temperature increases;¹²² this results in the formation of new microcavities of the fluctuation free volume (their nature has been considered in detail¹²³) and in an increase in f_{iv} . It is evident that the energy of thermal fluctuations is of the order of kT ; the energy of formation of a microcavity (ϵ_h) can be estimated from the equation

$$\epsilon_h = kT_g \ln \frac{1}{f_{iv}}. \quad (54)$$

Since the maximum f_{iv} value expected in the vitreous state is 0.159 (according to the most ‘rigorous’ estimates¹²⁴) and $T < T_g$, it is obvious that the energy of thermal fluctuations is insufficient for the formation of a microcavity.

The second point is determination of the f_{iv} value. This can be done by virtue of the following equation:

$$f_{iv} \approx 0.017 \frac{1 + \mu}{1 - 2\mu}. \quad (55)$$

For amorphous vitreous polymers, $f_{iv} \approx 0.050 - 0.090$,¹²¹ which is much greater than the value $f_{iv} \approx 0.025 \pm 0.003$, which has been found in terms of the Williams–Landell–Ferry (WLF) concept and is generally accepted for most polymers.¹¹⁸

Evaluation of some polymer properties requires not only the integral characteristic f_{iv} but also the parameters of a separate

microcavity of fluctuation free volume, which is traditionally represented as a sphere with volume V_h .¹¹⁹

Recalling that the fractal dimension of the polymer structure is in the range $2 \leq d_f \leq 3$, it can be suggested that the fluctuation free volume as a structural unit also possesses fractal properties. Using relations (55) and (23), the dependence of f_{fv} on d_f has been elucidated⁶⁰

$$f_{fv} \approx 8.5 \times 10^{-3} \frac{d_f}{3 - d_f}. \quad (56)$$

If the above assumption is correct, the following general relation should hold:¹²⁵

$$N_h \propto r_h^{D_{fv}}, \quad (57)$$

where N_h is the number of microcavities, r_h is their characteristic size, and D_{fv} is the fractal dimension of the fluctuation free volume.

As a first approximation, the r_h value can be expressed in terms of the microcavity volume as $V_h^{1/3}$, the volume being found from the equation

$$V_h = \frac{3(1 - \mu)kT_g}{f_{fv}E}. \quad (58)$$

Although this approximation introduces some inaccuracy to the quantitative results, it does not deteriorate the generality of the conclusions.

The number of microcavities N_h is expressed as the ratio¹¹⁹

$$N_h = \frac{f_{fv}}{V_h}. \quad (59)$$

Figure 22 presents the variation of $\ln N_h$ as a function of $\ln V_h^{1/3}$ for specimens of three epoxy polymers, EP-1, EP-2, and aged EP-2, which is designated by EP-3. It can be seen that the plots are linear; this is a typical feature of fractal behaviour. The D_{fv} values found from relation (57) for EP-1 and EP-2 were 5.9; that for EP-3 was 2.7.

It is clear that D_{fv} calculated in this way are averaged values; nevertheless, they provide grounds for an important conclusion: in the general case, a microcavity of fluctuation free volume can be represented by a D_{fv} -dimensional sphere, modelling by a three-dimensional sphere being a specific case. The D_{fv} values are close to the corresponding dimensions D_f of the regions of localisation of excess energy, which are determined from Eqn (39). In addition, D_f is equal to the automodelling coefficient A_i and, hence, to C_∞ . The fractal dimension D_{fv} interpreted in this way is closely related to the characteristics of the polymer structure.

Now we consider the energy criterion for the formation of a microcavity with the volume V_h . For this purpose, we use the concept of free fracture of solids,¹²⁶ according to which a limited amount of potential energy with density A^* can be accumulated in

a limited volume V and the formation of a new surface requires work equal to the product of the surface area S_n and the specific surface energy σ_n . In the case of free fracture,¹²⁷

$$A^*V = \sigma_n S_n. \quad (60)$$

As applied to the formation of a microcavity with the volume $V = V_h$, relation (60) can be represented as follows:⁸⁷

$$\frac{V}{S_n} = \frac{\sigma_n}{A^*}. \quad (61)$$

For a D_{fv} -dimensional sphere, it can be written that⁸⁷

$$\frac{V}{S_n} = \frac{r_h}{D_{fv}}. \quad (62)$$

The σ_n value can be represented as follows:¹¹⁹

$$\sigma_n = \frac{\epsilon_h}{2V_h^{2/3}}, \quad (63)$$

where ϵ_h is estimated from Eqn (54).

Finally, by determining A^* as the ratio

$$A^* = \frac{kT}{V_h}, \quad (64)$$

and using Eqns (61) and (63), we obtain

$$D_{fv} = \frac{4\pi T}{T_g \ln(1/f_{fv})}. \quad (65)$$

Since ageing can be interpreted as a tendency towards thermodynamic equilibrium,¹¹⁴ it is assumed that the condition $D_{fv} = 3$ corresponds to a certain quasi-equilibrium state of the polymer. This allows one to draw several conclusions. First, an increase in temperature, all other factors being the same, implies an increase in D_f and, hence, enhancement of the thermodynamic nonequilibrium of the polymer as a system. It follows from Eqn (39) that an increase in D_f is accompanied by an increase in μ ; this accounts for the well-known fact that the Poisson coefficient of polymers increases with temperature.^{74, 127, 128} Second, an increase in μ implies a decrease in the degree of local ordering of amorphous polymers,^{70, 129} which is manifested as a decrease in the density of the cluster network of entanglements V_{en} . In other words, an increase in V_{en} reflects the trend of a polymer towards thermodynamic equilibrium.¹¹⁴ Third, in the case where $D_{fv} = 3$, one can calculate the relative portion of the 'quasi-equilibrium' free volume (f'_{fv}); for the epoxy polymers in question, it falls in the range $\sim 0.028 - 0.042$, which is rather close to the f_{fv} value in the WLF equation mentioned above. Thus, the estimation of f_{fv} using Eqn (55) is correct and the considerable magnitudes of f_{fv} reflect a relatively high degree of thermodynamic nonequilibrium in epoxy polymers.

Let us consider the general statements of the concept of fluctuation free volume in relation to cross-linked systems. Figure 23a illustrates the relationship between the fractal dimensions of the regions of localisation of excess energy D_f [see Eqn (39)] and the fluctuation free volume D_{fv} [see Eqn (65)]. It can be seen that these two values are fairly close to each other.[‡] Thus, the f_{fv} value can actually be used to characterise the polymer structure.

The formation of a microcavity with the volume V_h requires local critical deformation ϵ_c ¹³⁰

$$\epsilon_c = \frac{1}{3} \frac{\ln(1/f_{fv})}{3\gamma}, \quad (66)$$

where γ is the Grüneisen parameter, characterising the anharmonicity of the intermolecular bonds in a polymer and the factor 3 was introduced under the assumption that a microcavity is three-dimensional. In view of this fact, this factor should be replaced by D_{fv} and thus Eqn (66) assumes the form

[‡] Some discrepancy is due to the fluctuation nature of free volume.

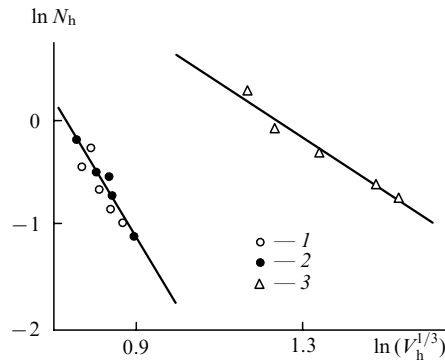


Figure 22. Number of microcavities of fluctuation free volume vs. their size for EP-1 (1), EP-2 (2) and EP-3 (3).

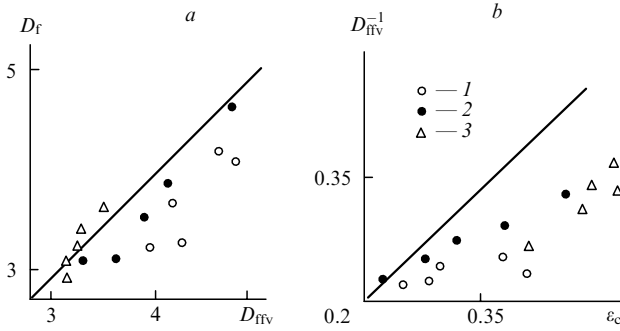


Figure 23. Relationships between the fractal dimensions of the regions of localisation of excess energy D_f and the fluctuation free volume D_{ffv} (a) and between the dimension of the fluctuation free volume and the critical deformation in the formation of microcavities ϵ_c (b) for EP-1 (1), EP-2 (2) and EP-3 (3).

$$\epsilon_c = \frac{\ln(1/f_{fv})}{3\gamma D_{ffv}}. \quad (67)$$

Thus, the more pronounced the fractality of the fluctuation free volume (the greater D_{ffv}), the smaller ϵ_c and the easier the formation of the microcavity. This fact is reflected in the dependence of ϵ_c on D_{ffv}^{-1} (Fig. 23 b). The γ value was found from the relation¹³⁰

$$\gamma \simeq 0.74 \frac{1 + \mu}{1 - 2\mu}. \quad (68)$$

It is noteworthy that the Grüneisen parameter varies in parallel with D_{ffv} and is related to the dimension of the fluctuation free volume by the following simple relation:

$$\gamma \simeq D_{ffv} - 1. \quad (69)$$

In other words, the Grüneisen parameter is also a fractal characteristic; for quasi-equilibrium conditions, $\gamma = 2$. The values $\gamma > 2$ mean an enhanced nonequilibrium character of the system.¹³¹

Figure 24 shows the dependence of γ on D_{ffv} and the dependence of V_h on K_{st} for three epoxy polymers. The V_h values for EP-1 and EP-2 vary from 0.97 to 7.31 nm³ but those for EP-3 are greater and lie in the range of 5.45–10.1 nm³. In terms of the free fracture concept, this implies that the formation of a microcavity in a system the state of which is close to quasi-equilibrium requires more thermal fluctuations with the energy kT than that in non-equilibrium systems (EP-1 or EP-2). The same requirement is valid for each particular composition, which is confirmed by the presence of a maximum on the dependence of V_h on K_{st} at $K_{st} = 1$. The degree of equilibration can be estimated as the difference

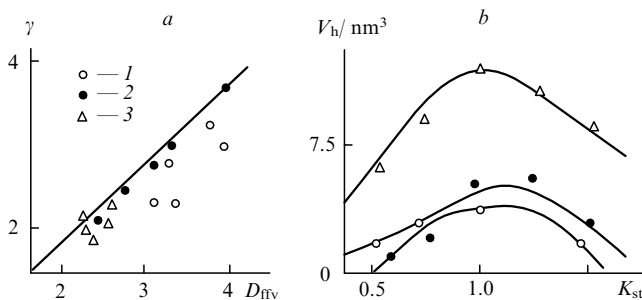


Figure 24. Relationship between the Grüneisen parameter γ and the dimension of the fluctuation free volume D_{ffv} (a) and the dependence of V_h on K_{st} (b) for EP-1 (1), EP-2 (2) and EP-3 (3).

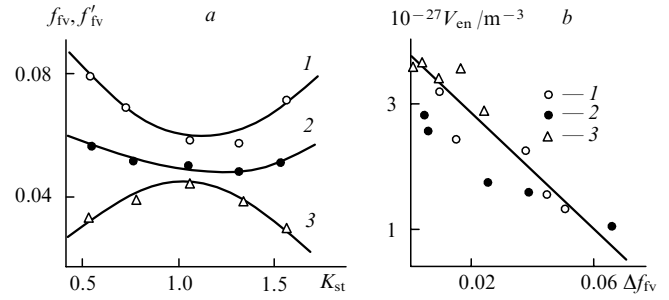


Figure 25. Variation of f_{fv} vs. K_{st} (a) and of the density of the cluster network of entanglements V_{en} vs. Δf_{fv} (b) for epoxy polymers.

(a): (1) EP-1, $f_{fv}(K_{st})$; (2) EP-1, $f'_{fv}(K_{st})$; (3) EP-3, $f_{fv}(K_{st})$; (b): (1) EP-1, (2) EP-2, (3) EP-3.

$$\Delta f_{fv} = f_{fv} - f'_{fv}. \quad (70)$$

The meaning of this estimate becomes evident if one compares the $f_{fv}(K_{st})$ and $f'_{fv}(K_{st})$ plots for EP-1 and EP-3 (Fig. 25 a). As noted above, samples with $K_{st} = 1$ are closest to the quasi-equilibrium state. The aged EP-3 samples at $K_{st} = 1$ have already reached this state and further ageing does not change the structure. The samples with $K_{st} \leq 0.50$ and those with $K_{st} \geq 1.50$ possess the lowest stability during physical ageing, which is displayed as the corresponding change in their properties. The decrease in the elastic modulus during ageing of EP-1 amounted to 1.7 GPa for $K_{st} = 1.50$ and 1.1 GPa for $K_{st} = 1.0$. Thus, by comparing the $f_{fv}(K_{st})$ and $f'_{fv}(K_{st})$ plots, one can demonstrate the degree of thermodynamic nonequilibrium of cross-linked systems and predict the possible changes in their structure and properties during physical ageing.

The closeness of a polymer to the equilibrium state can be characterised by the degree of ordering. Using the cluster model, this trend can be quantitatively described fairly easily in terms of the parameters V_{en} or ϕ_{cl} .^{57,132} The dependence of V_{en} on Δf_{fv} (Fig. 25 b) shows that the degree of local ordering can serve as an indication of the thermodynamic nonequilibrium of the polymer structure. Extrapolation of the straight line $V_{en}(\Delta f_{fv})$ to $\Delta f_{fv} = 0$ gives $V_{en} \simeq 3.8 \times 10^{27} \text{ m}^{-3}$, which is about 1.5 times lower than the maximum V_{en} value found as the ratio of the total length of the macromolecule per unit volume of the polymer to the length of the statistical segment.¹³³ This discrepancy stipulates the legitimacy of applying the term ‘quasi-equilibrium state’ to the polymer structure with $\Delta f_{fv} = 0$. It is clear that an equilibrium state implies that all macromolecules are packed in the regions of local ordering. It has been shown⁷⁰ that the condition $\Delta f_{fv} = 0$ cannot be attained for the epoxy polymers in question even for the maximum possible V_{en} value. Yet another important feature of the quasi-equilibrium state is temperature dependence of parameters, in particular, f_{fv} [see Eqn (65)]. When $V_{en} = 0$, the straight line $V_{en}(\Delta f_{fv})$ is extrapolated to $\Delta f_{fv} \simeq 0.077$, which also has a definite physical meaning. For $f'_{fv} = 0.035$ (see Fig. 25 a) and $\Delta f_{fv} \simeq 0.077$, the f_{fv} value is equal to 0.112, which is close to the fluctuation free volume at T_g .^{118,119} Thus, the destruction of clusters can be identified with glass transition of cross-linked polymers.

Thus, the above results point to the fractality of the fluctuation free volume in cross-linked polymers. In this connection, one important fact should be noted, which has not received adequate attention before. In accordance with Eqn (58), V_h decreases with an increase in f_{fv} . For pores with sizes of the order of several nanometers, it has been shown^{134,135} that

$$-\frac{dV}{d\rho} \propto \rho^{2-D'}, \quad (71)$$

where V is the total pore volume, ρ is the average pore radius, and D' is the fractal dimension of the structure of a porous material.

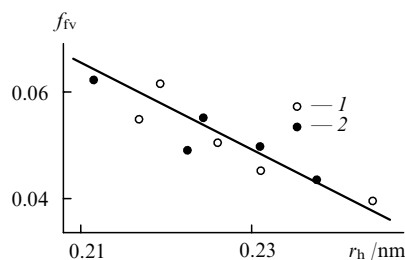


Figure 26. Relative fluctuation free volume f_{fv} vs. radius of the free volume microcavities r_h for EP-1 (1) and EP-2 (2).

According to different estimates, the linear sizes of microcavities of free volume r_h vary from 0.2 to 1.5 nm.^{136–142} If we assume that $V_h = f_{fv}$ and $r = r_h$, for Eqn (71) to have a physical meaning, it is evidently required that the slope of the $f_{fv}(r_h)$ plot be negative. The calculated D' values for EP-1 and EP-2 vary from 4.78 to 5.31, which is consistent with the above estimates of D_{fv} and D_f . Figure 26 presents the dependence of f_{fv} on r_h , which is linear and has a negative slope. Figure 27 illustrates the relationship between D_f and D' . It can be seen that D' values are regularly greater than D_f but both values vary according to the same pattern and the deviations do not exceed 25%. This also attests to the fractality of the free volume the dimension of which reflects the extent of ‘pumping’ of energy into the polymer and does not coincide with the corresponding dimension of the polymer structure.

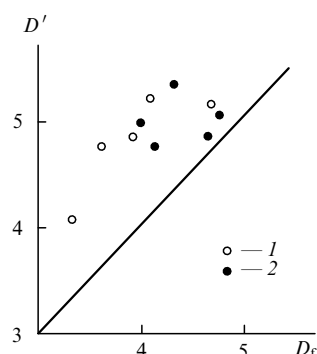


Figure 27. Relationship between the fractal dimensions D' and D_f calculated from Eqns (71) and (39), respectively, for EP-1 (1) and EP-2 (2).

Let us consider the influence of the ‘pumping’ of energy (mechanical or thermal) on the formation of free volume in epoxy polymers. Within the framework of the Frenkel’ kinetic theory,¹¹⁵ the radius of a microcavity of free volume r_h depends on the surface tension σ

$$r_h^2 = \frac{\varepsilon_h}{4\pi\sigma}. \quad (72)$$

Equation (72), which is an analogue of relation (63), permits calculation of σ provided that r_h and ε_h are known. The dependence of the σ values thus found on D_f for EP-1 and EP-2 is plotted in Fig. 28. An increase in D_f (enhancement of energy pumping from the outside) results in a decrease in σ , which facilitates the formation of a microcavity of the fluctuation free volume. Note that for $D_f = 7.7$, the σ value becomes equal to zero. This is unlikely from the physical viewpoint; nevertheless, it is evident that σ sharply diminishes on moving towards $D_f \approx 7.7$. This D_f value is matched by $\mu \approx 0.425$ [according to Eqn (39)], which corresponds to the mechanical⁷⁴ and thermal¹⁴³ glass transition process. It has been shown experimentally that V_h sharply increases (and, hence, σ decreases)¹³⁶ and the yield point increases¹⁴⁴ at T_g .

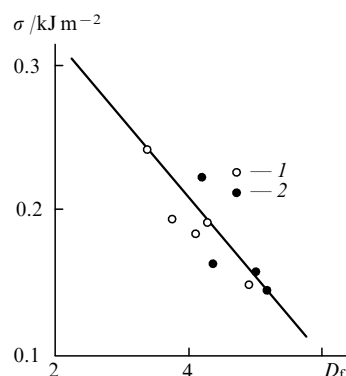


Figure 28. Surface tension vs. fractal dimension of the regions of localisation of excess energy for EP-1 (1) and EP-2 (2).

The variation of f_{fv} as a function of D_f is presented in Fig. 29. The straight line was drawn with the assumption that for $\mu = 0$ (which corresponds to close packing of an amorphous polymer¹²⁹), $D_f = 2$ and $f_{fv} = 0$, whereas for the maximum possible f_{fv} value at T_g [$f_{fv}^t \approx 0.159$ (see Ref. 124)], $\mu \approx 0.44$ and $D_f^t \approx 9.3$. The f_{fv} values found using relation (55) for EP-1 and EP-2 correspond to the proposed model. Thus, ‘pumping’ of energy into a polymer increases the dimensions of the regions in which it is localised and increases the fluctuation free volume.

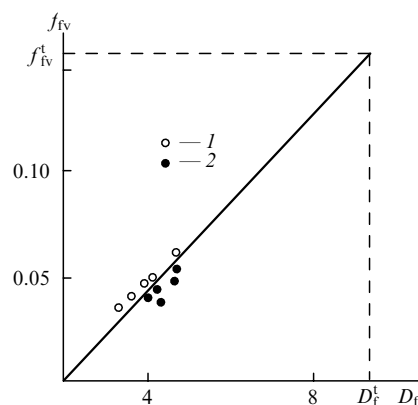


Figure 29. Relationship between the relative fluctuation free volume f_{fv} and the dimension of the regions of localisation of excess energy D_f . The points correspond to the calculation of f_{fv} from Eqn (55) for EP-1 (1) and EP-2 (2). The explanations are in the text.¹⁵³

Thus, the fluctuation free volume in vitreous polymers has a fractal structure; therefore, the microcavities that constitute the free volume can be modelled by a D_{fv} -dimensional sphere. The sizes of microcavities are controlled by the volume in which the energy of thermal fluctuations needed for their formation is accumulated. The absolute magnitudes of f_{fv} can characterise the thermodynamic nonequilibrium of the polymer structure. For quasi-equilibrium structures, it is assumed to be equal to f_{fv} in the known WLF equation. The dimension of the free volume regions (which coincides with the corresponding dimension of the regions of localisation of energy pumped from the outside) reflects the extent of energetic excitation of the polymer structure.

5. Fractal characteristics of polymers in time-dependent processes

Polymers obey the principle of temperature–time superposition,^{145, 146} according to which structural (including fractal) characteristics of polymers are functions of the time scale of testing. In this connection, we shall consider the influence of the

time factor on the fractal characteristics in processes typical of polymers such as thermal ageing or relaxation.

The dependences of the dielectric loss tangent ($\tan \delta$) on the Hausdorff dimension for several copolymers have different slopes at measurement frequencies of 1 and 10 kHz. This hampers correct prediction of $\tan \delta$. This difference can be easily explained in terms of the cluster model. The φ_{cl} value is a parameter of the order of the polymer structure;⁶⁰ due to the thermodynamic nonequilibrium of the structure, it is also a function of the time scale t . In the general case, the time-dependent order parameter $\varphi_{cl}(t)$ is determined as follows:¹⁴⁷

$$\varphi_{cl}(t) = \varphi_{cl}^0 \exp\left(-\frac{t}{\tau_0}\right), \quad (73)$$

where φ_{cl}^0 is the φ_{cl} value at very large t and τ_0 is the relaxation time under normal conditions.

If the time scale of the experiment is expressed in terms of π/ω (ω is the frequency of measurements) and the relaxation time is assumed to be $\tau \approx 10$ ms, the φ_{cl} value can be estimated as a function of frequency and, hence, different D values for frequencies of 1 and 10 kHz can be obtained. An increase in D (decrease in t) results in higher φ_{cl} [according to Eqn (73)] and in lower D .¹⁴ Therefore, the dependence of $\tan \delta$ on D is described by one straight line for both frequencies mentioned above.²⁶ Thus clusters can be generally defined as regions in which relaxation processes are impossible.

Physical ageing of amorphous vitreous polymers consists in the variation of the structure and properties with time, which reflects the thermodynamically nonequilibrium nature of these polymers.¹¹⁴ At relatively low temperatures (about room temperature), this process is fairly slow; it takes several years for substantial changes in the properties to occur.^{94, 148} Therefore, forecasting of these phenomena should be performed with allowance for both spatial and temporal disorder of systems. The spatial non-uniformity of the structure of amorphous vitreous polymers accounts for the rather broad range of the rates of relaxation processes. Spatial disorder results in temporal disorder. The variation of the properties and structure of polymers during ageing can be described quantitatively within the framework of fractal analysis.

Study of the reaction dynamics in disordered systems has shown that for most reactions at long times, subordination expressed by the following general relation is obeyed:¹⁴⁹

$$\Phi \propto t^{\alpha\gamma}, \quad (74)$$

where Φ is an arbitrary function dependent on time t and α and γ are coefficients taking into account the spatial and temporal disorder.

As applied to physical ageing, the variation of structure with time can be described, on the basis of general relation (74), in the following way:¹⁵⁰

$$V_{cl} = C V_{cl}^0 t^{\alpha\gamma}, \quad (75)$$

where V_{cl} and V_{cl}^0 are the densities of the cluster network of entanglements in the aged and initial polymers, respectively; C is a proportionality coefficient. The index α can be defined in terms of fractal analysis as the difference $d_f - 2$, where d_f is the fractal dimension of the structure of the initial epoxy polymer, with allowance for the following considerations: the $2 < d_f \leq 3$ range characterises the degree of disorder of the polymer structure;¹⁵¹ most information on this point is carried by the fractional part of d_f : the greater the magnitude of d_f , the lower the local order and, hence, the higher the spatial disorder of the system.¹⁵²

The quasi-equilibrium state of polymers is characterised by $d_f \approx 2.5$. This value corresponds to a fully relaxed polymer with a narrow size distribution of free volume cavities¹⁵³ and, hence, to the least temporal disorder, characterised by a spectrum of relaxation times. Therefore, the following approximation has been used:¹⁵⁰

$$\gamma = d_f - 2.5. \quad (76)$$

Thus, Eqn (75) can be finally written in the form

$$V_{cl} = V_{cl}^0 C t^{(d_f-2)(d_f-2.5)}, \quad (77)$$

where the coefficient C determined empirically is equal to ~ 0.14 and the time of ageing is expressed in seconds.

Figure 30 shows the dependences of φ_{cl} on K_{st} for the initial (EP-2) and aged (EP-3) epoxy polymers. In the case of EP-3, the φ_{cl} values determined experimentally and calculated using Eqn (77) are given. It can be seen that the experimental and calculated values are in good agreement. The maximum deviations for K_{st} equal to 0.50 and 1.50 do not exceed $\sim 25\%$. It is assumed¹⁵⁰ that the main reason for the inaccuracy is the high power dependence of V_{cl} on d_f in Eqn (77).

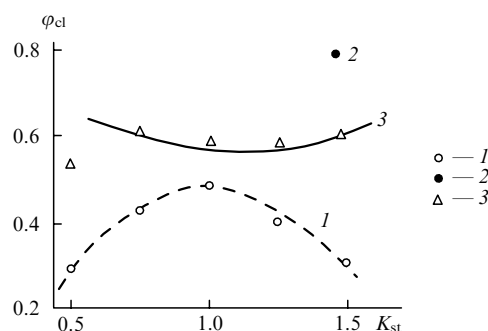


Figure 30. Relative portion of clusters φ_{cl} vs. the curing agent: oligomer ratio K_{st} for EP-2 (1) and EP-3 (2, 3); (1, 2) experimental data, (3) calculation using Eqn (77).¹⁵⁰

Yet another important aspect of physical ageing is also associated with the dependence of φ_{cl} on K_{st} (see Fig. 30). The ageing rate expressed as the difference between the φ_{cl} values for EP-2 and EP-3 varies substantially for different K_{st} (and, hence, for different chemical cross-linking densities v_s). The minimum ageing rate is observed for a system with $K_{st} = 1.0$;¹⁵² deviations from this value towards both greater and lower values result in an increase in the ageing rate.¹⁰¹ This is due to an increase in both α and γ [see Eqn (77)] or, in other words, to an increase in the fractal dimension of the structure d_f .

Parameters which vary during physical ageing include not only supermolecular structure characteristics (d_f and D_f) but also the statistical chain flexibility index C_∞ . Using Eqns (39) and (41), it can be written that

$$A_i = C_\infty = D_f = 2 \frac{1 - \mu}{1 - 2\mu}. \quad (78)$$

The physical ageing results ultimately in the formation of similar structures for all the epoxy polymers considered, irrespective of the density of chemical cross-linking points (v_s varies by approximately an order of magnitude).¹⁵⁴ Naturally, this structure equalisation also determines substantial convergence of the properties of EP-2 and EP-3.⁹⁴

From the practical viewpoint, it is important to predict the properties of polymers during physical ageing. A procedure suitable for this purpose has been reported.¹⁵⁰ This procedure is based on Eqn (77). Knowing the V_{cl} and C_∞ values, one can estimate D_f and calculate E .¹⁵⁵ Then the yield point σ_p ^{142, 148} and some characteristics of polymers^{64, 156} can be determined.

In recent years, considerable attention has been paid to investigation of the relaxation processes in complex condensed systems. An example of this type of system is amorphous-crystalline polyethylene, the structure of which under normal conditions consists of crystalline regions, regions of local ordering and a devitrified loosely packed matrix.^{157, 158} The interest in these

studies is caused by the experimental fact that the correlation functions for many different systems vary in accordance with the same exponential dependence

$$\varphi(t) = \exp \left[- \left(\frac{t}{\tau} \right)^\beta \right], \quad 0 < \beta < 1. \quad (79)$$

The parameters β and τ depend both on the material and on the environmental conditions, for example, temperature.

The law described by Eqn (79) was first proposed by Kohlrausch and has later been used by Williams and Watts to describe the dielectric relaxation in polymers (M Schlesinger, J Klafter, see Ref. 149, p. 553). The main difficulty in the case of polymers is to identify the parameters of Eqn (79) in terms of characteristics describing the polymer structure. This identification has been performed within the framework of fractal analysis.³⁹

In the impact testing of polymers, the elastic modulus decreases with an increase in the time scale of testing (in the case of brittle fracture, this is time to fracture t') and can be described by the empirical relation^{159, 160}

$$E = E_0(t')^{-m}, \quad (80)$$

where E_0 is the 'unity' modulus, *i.e.* the E value for $t' = 1$ on the time scale chosen, and m is an empirical index characterising the degree of completeness of relaxation processes.

Figure 31 shows the variation of E as a function of t' corresponding to Eqn (80) for high-density polyethylene samples with different lengths of a sharp notch (an increase in the length decreases t') at a testing temperature of 293 K. The slope of the straight line can be used to estimate the index m , while extrapolation of the plot to $t' = 1$ gives the E_0 value. It should be noted that at certain t' values (for example, τ), the variation of $\ln E$ vs. $\ln(1/t')$ has a break — at $t' < \tau$ the elastic modulus increases faster than at $t' > \tau$, which reflects an increase in m . This finding is related to the extent of completeness of relaxation processes: at $t' > \tau$ this extent is high and, correspondingly, the increase in E is insignificant.

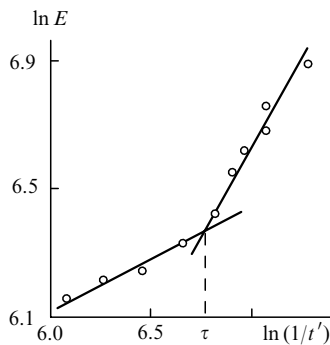


Figure 31. Elastic modulus E vs. time to fracture t' [see Eqn (80)] for high-density polyethylene samples with a sharp notch; $\tau = \tau_0$ is relaxation time.¹⁵³

The difficulty in describing the variation of E according to Eqn (80) is due to the presence of two empirical constants (E_0 and m), which, moreover, can change discretely. Therefore, an alternative approach based on the use of the Kohlrausch equation (79) has been chosen.¹⁵³ To describe E , this equation should be written in the form

$$E = E'_0 \exp \left[- \left(\frac{t'}{\tau_0} \right)^\beta \right], \quad 0 < \beta < 1, \quad (81)$$

where E'_0 is a constant.

Let us consider the physical meaning of the parameters appearing in Eqn (81). It is evident that the τ value can be taken

as τ_0 (see Fig. 31). The constant E'_0 determines the maximum elastic modulus $E_{\max}$ which can be attained for a given polymer without relaxation. The range of variation of this parameter for very high testing frequencies (several megahertz) was found¹⁶¹ to be 1.1–2.6 GPa for high- and low-density polyethylene. Finally, the index β , characterising the width of the relaxation spectrum (spatial disorder of the system), can be associated with the fractional part of d_f , *i.e.* it is taken to be equal to $d_f - 2$. Note that both β and $d_f - 2$ vary over the same limits. Thus, the final form of the Kohlrausch equation for determining the elastic modulus of polymers under high-speed loading (brittle fracture) can be written as follows¹⁵³

$$E = E_{\max} \exp \left[- \left(\frac{t'}{\tau} \right)^{d_f - 2} \right], \quad 0 < (d_f - 2) < 1. \quad (82)$$

Figure 32 shows the dependences of the E values, both experimental and calculated from Eqn (82), on the sharp notch length l for high-density polyethylene samples at different temperatures. Good agreement between the theoretical and experimental results is obvious.

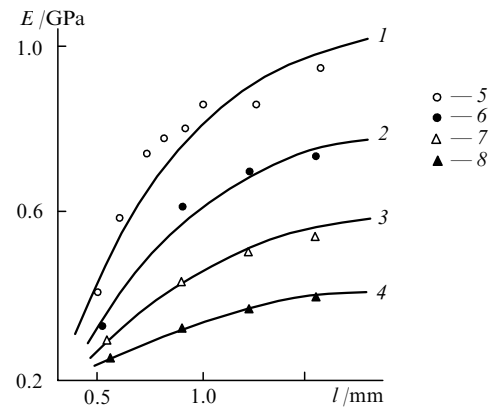


Figure 32. Experimental (1–4) and calculated [Eqn (82)] (5–8) elastic moduli E vs. length of the sharp notch l for high-density polyethylene at testing temperatures of 293 (1, 5), 313 (2, 6), 333 (3, 7) and 353 K (4, 8).¹⁵³

Thus, methods of fractal analysis in combination with the cluster model of the structure of amorphous polymers provide a quantitative description of time-dependent processes. The fact that the fractal dimension of the structure d_f takes into account both the spatial and temporal disorder accounts for the simplicity of the resulting equations.¹⁵⁰

III. Modelling of the structure and properties of polymers

1. Modelling in terms of the percolation theory

Percolation models are widely used to describe critical phenomena¹⁶² including those in polymers.^{162–166} Percolation clusters are homogeneous fractals when $x \neq x_c$ (x is the current coordinate, x_c is the coordinate of the percolation transition). For example, the structure of vitreous polymers is a fractal when $T \neq T_g$ or, with allowance for the foregoing, when $T < T_g$.

It should be borne in mind that the fractal properties of the polymer structure are due to the presence of the cluster structure or, more precisely, of 'frozen' ordering. However, as has already been mentioned, the magnitude of the fractal dimension of the structure d_f for amorphous polymers is debated, the overall range being $2 \leq d_f \leq 3$.¹²⁵ Thus on the basis of theoretical statements of Alexander and Orbach,⁴³ it has been concluded¹⁶⁷ that for an ideal disordered linear polymer, d_f is equal to 2, while for real amorphous polymers, this value is 2.0–2.2. Let us make several rather simple estimates of d_f for epoxy polymers EP-1 and EP-2. For a percolation system, the following relation holds:¹⁶²

$$d_f = d - \frac{\beta}{\nu}, \quad (83)$$

where d is the dimension of the Euclidean space in which the fractal is inserted and β and ν are critical indices of a percolation system related to each other as

$$d\nu = 2\beta + \gamma_c, \quad (84)$$

where γ_c is also a critical index of the percolation system. The parameters calculated from Eqn (83) are listed in Table 2.

Table 2. Parameters of percolation systems for epoxy polymers.

Parameter	Experiment		Calculation using Eqn (83)
	EP-1	EP-2	
ν	0.67	1.15	0.88
β/ν	0.537	0.504	0.455
d_f	2.46	2.50	2.545

The evaluation of the index ν for EP-1 and EP-2 for $d = 3$ using Eqn (84) and the β and γ_c values determined previously gives 0.67 and 1.15, respectively, which is consistent with the theoretical value $\nu = 0.88$ (see Table 2).

The d_f values for epoxy polymers estimated using Eqn (23) fall in the range from 2.56 to 2.73, which is in good agreement with the estimates made in this review but is substantially greater than has been assumed previously.^{43, 167}

The following ratio for percolation clusters has been reported:

$$d_{\text{super}} = \frac{d_f}{d_s}, \quad (85)$$

where $d_{\text{super}} > 1$ is so-called superlocalised index.

Using the d_{super} and d_s values found experimentally for epoxy polymers based on bisphenol A,^{167, 168} we calculated d_f , which proved to be 2.55. This value is close to the above estimates. Note that the application of Eqn (85) to the calculation of d_{super} of epoxy polymers became possible owing to the representation of their structure as a percolation system.

The d_f value can also be estimated without experimental d_s but using only the index d_{super} . For example, the random walk dimension d_w can be represented, with allowance for Eqn (85), in the following form:

$$d_w = 2d_{\text{super}}. \quad (86)$$

The d_f values for the epoxy polymer at $d_{\text{super}} = 1.85$ ¹⁶⁷ amounted to 2.47 and 2.70 in accordance with the Alexander–Orbach and Aharoni–Stauffer hypotheses,⁴⁸ respectively. These values are close to the estimates made using Eqn (23).¹⁶⁷

The fractal dimension is determined by the disorder which is generated by deterministic chaos. This statement can be expressed in the analytical form¹⁶⁹

$$d_f = \frac{S}{\lambda}, \quad (87)$$

where S is the entropy of the system, λ is the Lyapunov index.

The entropy change ΔS in a chaotic process can be determined using the following simple formula:^{170, 171}

$$\Delta S \approx 3kf_{iv} \ln f_{iv}, \quad (88)$$

where f_{iv} is determined from Eqn (55) and k is the Boltzmann constant.

Figure 33 shows the variation of d_f [calculated in terms of Eqn (23)] as a function of ΔS [calculated using Eqn (88)] for the epoxy polymers under consideration. This plot has some interesting features. First, extrapolation of the $d_f(\Delta S)$ straight line to $\Delta S = 0$ yields the value $d_f = 2$. Relation (88) indicates that the condition $\Delta S = 0$ is matched by $f_{iv} = 0$. This implies close packing

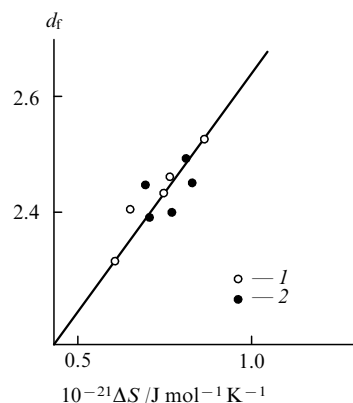


Figure 33. Fractal dimension d_f of the structure vs. entropy for EP-1 (1) and EP-2 (2).¹⁷⁰

of the structure of epoxy polymers. In other words, the value $d_f = 2$ is attained for an amorphous polymer in the case of close packing rather than in the case of ideal disorder, as has been suggested in a previous publication.¹⁶⁷ Second, $d_f = 3$ is attained at a ΔS value corresponding to $f_{iv} \approx 0.157$. This is known to be the greatest theoretical value relative to the free volume at T_g .¹²⁴ This means that $d_f = 3$ corresponds to the devitrified state of the polymer, *i.e.* to destruction of the local ‘frozen’ order. This fact confirms the relationship between local order and fractality of amorphous polymers. Third, in accordance with relation (87), the linear dependence of d_f on ΔS means that $\lambda = \text{const}$. Thus, the chaotic component of the dynamics of structure formation is the same for the epoxy polymers considered.¹⁷²

Thus, the structure formed in epoxy polymers at the glass transition temperature T_g is a percolation cluster, which is described adequately in terms of the cluster model.^{57, 173} Therefore, it can be assumed that glass transition of a polymer is a phase transition and ϕ_{cl} is an order parameter. In addition, this fact can serve as evidence confirming fractality of the structure of network polymers (for $T < T_g$) in the range of length scales of ~ 0.3 – 5.0 nm. The fractal dimension of the structure of epoxy polymers is much greater than it has been believed previously (see, for example, Ref. 60); it is determined by the disorder generated by deterministic chaos. The loss of fractality by the epoxy polymer structure, *i.e.* the situation when $d_f = d$ is attained at the glass transition temperature.

It is worth noting that the model of percolation cluster proposed by Kozlov *et al.*^{166, 170} is similar in essence to the concept of critical thermal transition.¹⁹ According to this concept, the portion of system elements belonging to the greatest cluster is proportional to the order parameter, which varies near the critical temperature T^* as ε^β , where $\varepsilon = (T - T^*)/T^*$.

2. The model of diffusion-limited aggregation

The general description of the models of irreversible aggregation has been reported in several publications.^{12, 162, 174} Here we shall consider particular aspects of using the model of diffusion-limited aggregation (DLA) for describing the structure of amorphous polymers. Note that the computer simulation procedures, widely used for this purpose, should be made more specific. If the cluster model of the structure of amorphous polymers^{173–175} can be described as the Witten–Sander (WS) cluster, this means that the model and the WS cluster belong to the same class of universality.

There exist numerous reasons for representing the structure of an amorphous polymer as WS clusters and for assigning them to one class of universality. These reasons have been considered in detail;⁶⁰ here we mention only three most important ones.¹⁷⁶ The first reason is that the aggregation mechanism belongs to one class of universality; for WS clusters, this is attachment of separate particles to the growing clusters (aggregation of the particle–

cluster type). In terms of the cluster model, this mechanism is attachment of a statistical segment to a region of local order; this event is equivalent to the ‘collapse’ of a microcavity of the fluctuation free volume.^{57,121} The second reason follows from the first one: due to the identical aggregation mechanisms, the structures of amorphous polymers and the WS clusters have the same scaling indices, namely, the dimensions d_f (see Refs 170 and 171) and D (see Ref. 172), respectively. The third reason is as follows. It is known⁴⁴ that during the synthesis of polymers, the class of universality changes in the gelation point, namely, the cluster–cluster mechanism is replaced by the particle–cluster mechanism; the latter affords WS clusters.

The model representation (in terms of the DLA model) made it possible to describe the structures of EP-1 and EP-2; this was done using the same scaling index, namely, the dimension d_f .¹⁷⁵ It should be mentioned that the word ‘cluster’ is interpreted in different ways in the cluster model¹⁷⁷ and in the WS cluster model. In terms of the latter, the term ‘cluster’ denotes both the region of local ordering and the chains protruding from it, while in the former case, only statistical segments incorporated in the region of local ordering are meant. It is evident that the structure of a polymer sample cannot be regarded as a single WS cluster. Therefore, by analogy with Belousov *et al.*,¹⁷⁷ who proposed a modified variant of the WS model, we represent the structure of epoxy polymers by a set of WS clusters, the size of each cluster ranging from l_{st} to R_{cl} . Therefore, the model of multiple growth sites is the most plausible modification of the WS model. According to the WS model, the growth of a WS cluster takes place on a large number of seeds, the cluster size R_{cl} being related to the concentration of free diffusing particles N in the following way:

$$N \simeq R_{cl}^{D-d}. \quad (89)$$

Only those statistical segments that are located in the loosely packed matrix are able to join the region of local ordering. An increase in the degree of local ordering decreases the temperature; for $R_{cl} = \text{const}$, this means a decrease in the difference $D-d$ or a decrease in D . The N value was taken to be equal to the product of the number of particles (statistical segments) per unit volume and the proportion of the loosely packed matrix. Figure 34 shows the plots for the variation of the fractal dimensions of the epoxy polymer structures¹⁵⁶ and of the WS cluster, calculated using relation (89), *vs.* the curing agent : oligomer ratio. One can notice good correspondence between d_f and D .¹⁷⁵

Thus, a modified version of the particle–cluster aggregation model¹⁷⁸ allows the structures of network polymers to be described in terms of D . This stipulates the assignment of the structure of network polymers to the given class of universality and, hence, description of its properties by relations developed for this class of universality.¹⁷⁵

Description of the local ordering of the structure of amorphous polymers (in relation to polycarbonate and high-density polyethylene) in terms of the WS model has been reported.¹⁷⁶ The following equation characterises the variation of the density of the

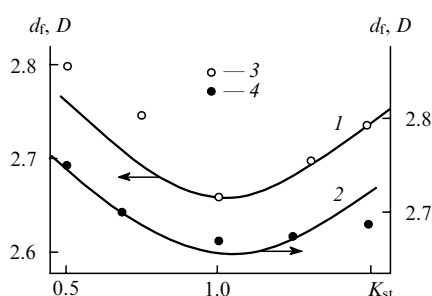


Figure 34. Fractal dimensions of the structure d_f (1, 2) and of the WS clusters D (3, 4) *vs.* the curing agent : oligomer ratio K_{st} for EP-1 (1, 3) and EP-2 (2, 4).¹⁵⁶

WS cluster ρ_{ws} as a function of its radius R_{ws} and the dimension D :¹⁷⁹

$$\rho_{ws} = \rho \left(\frac{R_{ws}}{a} \right)^{D-d}, \quad (90)$$

where ρ is the density of the material of the WS cluster in the state of close packing, a is the lower boundary of the fractal behaviour of the WS cluster, which can be identified with the length of an elementary unit in the polymer chain.

A WS cluster obeys the relations $D < d$ and $\rho_{ws} < \rho$, which determine the condition $a < R_{ws}$. Replacement of the signs in the first two inequalities by equality signs implies transition of the cluster to another class of universality, for example, transition to the Eden cluster.⁸⁷ Meanwhile, since $\rho_{ws} \neq 0$ and $\rho \neq 0$, a cannot be equal to zero. Thus, a compact region ($D \simeq d$) with size a , identified as a region of local ordering for the structure of an amorphous polymer, always exists in the centre of the WS cluster. This statement is a necessary condition for the existence of the WS cluster.¹⁸⁰ Two remarks on this point are pertinent.

First, the cause for the appearance of the compact region at initial stages of formation of a WS cluster can be easily understood. Indeed, the fractal nature of the WS cluster is determined by the shielding effect of its ‘branches’, which prevent the access of particles into the inner regions of the cluster.^{180,181} However, in initial stages of the growth, these ‘branches’ are poorly developed and the shielding effect is low. Second, the polymer structure, as any real (physical) fractal, possesses fractal properties only in a particular range of length scales.⁸⁷ It has been shown experimentally^{167,182} that this range for polymers is from several Ångström to several tens of Ångström. This implies the presence of a density gradient in the polymer in this range of length scales, which, in turn, means alternation of blobs and rarefied sections in the material.¹⁸³ The cluster model^{173,177} satisfies this condition, whereas, for example, the ‘felt’ model of the polymer structure proposed by Flory¹¹³ cannot account for the experimentally observed fractal properties.^{167,182,183}

Thus, interpretation of the structure of an amorphous polymer as a WS cluster (more precisely, as a set of these clusters) assumes necessarily the existence of regions of local order. This has been confirmed¹⁷⁶ by comparing the a values calculated from Eqn (90) and the size of the region of local order r_{cl} (Fig. 35). The r_{cl} value can be found from the following equation (under the assumption of close packing):¹⁸⁴

$$r_{cl} = \left(\frac{n_{cl} S}{\pi \eta} \right)^{1/2}, \quad (91)$$

where n_{cl} is the number of statistical segments in the cluster, η is the density of packing of the element, equal to 0.74.¹⁸⁴

Figure 36 shows the variations of the size of the regions of local order r_{cl} in the cluster model¹⁷³ and the compact regions a in the WS model *vs.* testing temperature for polycarbonate and high-density polyethylene. In studies by Kozlov *et al.*,^{176,185} the density of the loosely packed polymer matrix, which coincides with the density of the polymer above the glass transition (melting) temperature, was taken as ρ_{ws} and the density of the crystalline

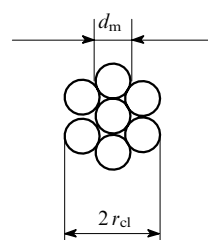


Figure 35. Cross-section of the region of local order incorporating seven statistical segments (d_m is the diameter of the polymer macromolecule).¹⁷⁵

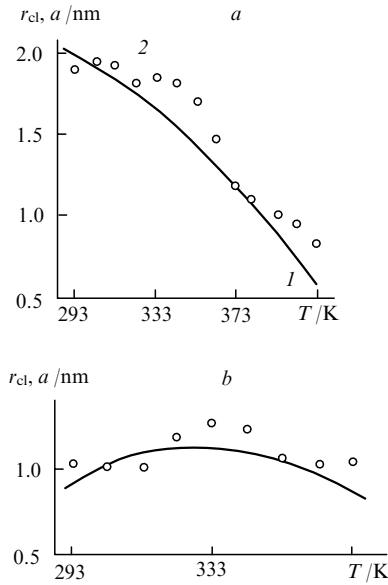


Figure 36. Size of the regions of local ordering r_{cl} (curve) in the cluster model and size of the compact regions a (dots) in the WS model vs. temperature for polycarbonate (a) and high-density polyethylene (b).

regions of polycarbonate and polyethylene was used as ρ . In addition, it was assumed in calculations that

$$R_{cl} = R_{WS}, \quad (92)$$

$$D = d_f. \quad (93)$$

The absolute magnitudes and the patterns of temperature variation of the parameters r_{cl} and a are in good agreement. Some scatter in the a values relative to r_{cl} is due to the inaccuracy in the determination of d_f using Eqn (23), caused by the power dependence of a on D , which markedly affects the accuracy of comparison.

Thus, it can be inferred that experimental results also indicate the obligatory existence of regions of local order in the structure of an amorphous polymer in terms of the DLA model. The structure of amorphous polymers can also be studied using the method of autocorrelation functions¹⁷⁶

$$C(r) = \langle p(r') - p(r' + r) \rangle, \quad (94)$$

where $p(r')$ and $p(r' + r)$ are probabilities that particles composing a cluster are located at points r' and $r' + r$ (the probability is equal to unity when the point does contain a particle and to zero when no particle is present). The autocorrelation function for distances r greater than several lattice spacings can be represented by the scaling relation¹⁸⁶

$$C(r) \propto r^{-\alpha}, \quad (95)$$

where

$$\alpha = d - D. \quad (96)$$

In the case of a linear autocorrelation function, having determined α , one can estimate the fractal dimension D of the object.

The autocorrelation function for the structure of an amorphous polymer (in particular, polycarbonate) is shown schematically in Fig. 37; the density variation is presented as a function of distance, the reference point ($r = 0$) being placed at the centre of a local order region (see Fig. 35). Over an interval from 0 to r_{cl} the ρ value remains constant and equal to the density of the region of local order, which has been assumed, as a first approximation, to be equal to the ρ_{cr} value for crystalline polycarbonate.¹⁸⁷ In the range from r_{cl} to R_{cl} , the density is supposed to decrease linearly to reach ρ_{min} , which is estimated as follows. Litt *et al.*¹⁸⁷ have reported the averaged density of amorphous polycarbonate ρ_a ,

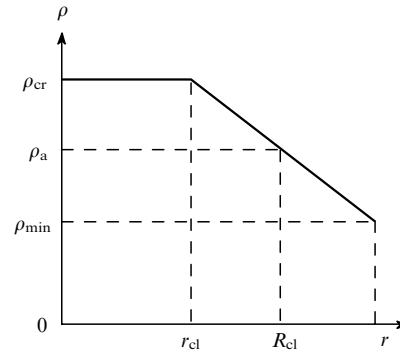


Figure 37. Autocorrelation function $\rho(r)$ for polycarbonate. The explanations are in the text.

which corresponds to the centre of the sloping section in Fig. 37. From simple geometric considerations, we obtain

$$\rho_{min} = \rho_a - (\rho_{cr} - \rho_a). \quad (97)$$

Now one can estimate the α value from the relation

$$(\rho_{cr} - \rho_{min})^{-\alpha} \simeq \left(\frac{R_{cl}}{2} - r_{cl} \right)^{-\alpha}, \quad (98)$$

and then calculate the d_f value for the polymer structure using Eqn (96) because modelling of this structure by a WS cluster assumes that equality (93) is valid.¹⁷⁸

The temperature dependences of the fractal dimension of the polycarbonate structure obtained experimentally and calculated in terms of the WS model taking account of relations (95) and (98) are presented in Fig. 38. It can be seen that the results correspond rather well to each other. However, the agreement can be improved by using so-called 'true' yield point. Kozlov *et al.*¹⁶⁶ determined d_f for polycarbonate at 293 K using five different procedures; the average value was found to be $d_f \simeq 2.51$. This result is in good agreement with the value $d_f \simeq 2.56$ determined for 293 K in terms of the WS model.

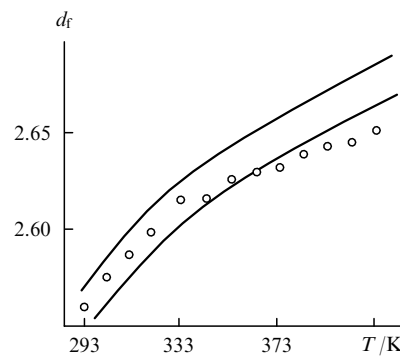


Figure 38. Fractal dimensions d_f of the structures of polycarbonate (1, 2) and WS cluster (3) vs. temperature. Determined with allowance for real (1) and 'true' (2) yield point.

Recalling that the quasi-equilibrium state of a polymer structure is characterised, in the general case, by $d_f = 2.5$, the same fractal dimension is typical of a WS cluster in a three-dimensional space when $N \rightarrow \infty$.¹⁸⁶ Therefore, below we consider the correspondence between the conditions of formation of a quasi-equilibrium state in the cluster model of an amorphous polymer structure and in the WS model. The modification of the WS model discussed above (growth on a large number of 'seeds')¹⁷⁷ uses the term 'diffusion distance' ξ , which depends on the local environment of each 'seed'. The growth of a WS cluster

continues until the condition $\xi \simeq R_{cl}$ is attained. The ξ and R_{cl} values are related to the concentration of free particles (c_{fr}) in the following way:¹⁷⁸

$$\xi \simeq c_{fr}^{-1} R_{cl}^{D-d+2}. \quad (99)$$

Taking into account the condition for termination of the cluster growth, it can be written that

$$c_{fr} \simeq R_{cl}^{D-d}. \quad (100)$$

This relation allows one to determine the concentration of free particles at the moment when the WS cluster stops growing having reached the size R_{cl} (subsequently, this concentration is designated by c_{WS}) or when the quasi-equilibrium state in terms of the WS model has been attained because in this case, too, the diffusion growth is restricted by interaction of the neighbouring WS clusters.

The concentration of particles in the cluster can be determined in terms of the cluster model.¹⁷³ Using relations (45) and (53), d_f can be related to the fraction of clusters ϕ_{cl} . Assuming that $d_f = 2.5$, one can estimate the ϕ_{cl} value for the quasi-equilibrium state of polymers.¹⁵

The R_{cl} value in the model¹⁷⁸ is limited by the number of 'seeds', which is, in turn, equal to the number of WS clusters, n_{WS} . According to the cluster model, the number of statistical segments incorporated in the regions of local order per unit volume of the polymer is assumed to be equal to the density of cluster network V_{cl} . The functionality F of such a region is the number of chains protruding from it. Since this region (cluster) is an analogue of a crystallite with extended chains, the number of segments in one cluster is equal to $F/2$. The number of regions of local order N_{cl} , equal to n_{WS} , in unit volume of the polymer can be found from the equation¹¹³

$$N_{cl} = \frac{2V_{cl}}{F}. \quad (101)$$

In addition to the cluster network of entanglements, polymers are known to contain a network of traditional 'loops'; unlike the cluster network, the latter is retained above T_g .¹⁴⁶ The numbers of entanglements in this network, determined above T_g , have been reported (see, for example, Refs 62, 76, 188). The density of the network of these 'loops' (V_{en}) can be found from the equation

$$V_{en} = \frac{\rho N_A}{M_{en}}, \quad (102)$$

where M_{en} is the molecular mass of the chain between entanglements.

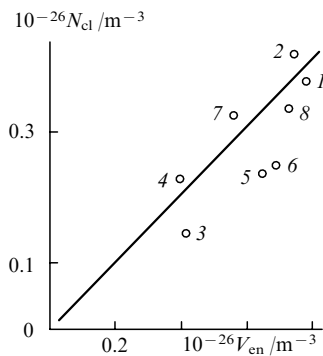


Figure 39. Relationship between the densities of clusters N_{cl} and the network of macromolecular 'loops' V_{en} for various polymers; (1) poly(ethylene terephthalate), (2) polyamide-6, (3) polyethylene, (4) polypropylene, (5) polystyrene, (6) poly(methyl methacrylate), (7) poly(vinyl chloride), (8) polycarbonate.

Figure 39 illustrates the relationship between the N_{cl} and V_{en} values for eight polymers. It can be seen that these parameters correspond to each other both in magnitude and in the pattern of variation. The rather large scatter is due to the discrepancies between the M_{en} values taken from different sources for the same polymer [for instance, for polyethylene, $M_{en} = 737 \text{ g mol}^{-1}$ (see Ref. 62) or 1900 g mol^{-1} (see Ref. 188)]. Nevertheless, under the assumption that $N_{cl} \simeq V_{en}$, the V_{en} value can be identified as the density of 'seeds' and the R_{cl} value can be found using Eqn (30).

The use of dimensional R_{cl} values in relation (100) results in the c_{WS} value being dependent on the dimension of R_{cl} . Therefore, the lower limit (b) at which the fractal properties are manifested ($b \simeq 0.5 \text{ nm}^{173}$) was chosen as the scale, and the dimensionless parameter R_{cl}/b was used in Eqn (100). When a different b value is employed, c_{WS} somewhat changes but the trend of its variation is retained.

It has been shown¹⁸⁹ that the minimum value $d_{fmin} = 2.5$ is typical only of polymers with $C_\infty = 3$. The d_{fmin} value can be determined by modification of the equation¹⁹⁰

$$\frac{d_{fmin}}{3(3 - d_{fmin})} + \frac{4}{3} = C_\infty. \quad (103)$$

For polymers with $C_\infty > 3$, the calculation gives incorrect ϕ_{cl} values (greater than unity). Therefore, the d_{fmin} values found for polymers using Eqn (103) are greater than 2.5. Thus, the chain rigidity has a substantial influence on the formation of the polymer structure.

Only segments incorporated in the loosely packed matrix have the opportunity to join the regions of local ordering. Thus, in terms of the WS model, it is these segments that should be considered as free particles. Therefore,

$$c_{sf} = 1 - \phi_{cl} = \phi_{lp},$$

where ϕ_{lp} is the volume fraction of the loosely packed matrix.

Figure 40 illustrates the good correspondence between the c_{WS} and c_{sf} values for twelve polymers, which attests that the interpretations of the quasi-equilibrium state of the polymer structure in the cluster model¹⁷³ and in the WS model¹⁷⁸ are equivalent. The c_{WS} values are somewhat greater than c_{sf} because the scale b was chosen arbitrarily.

Thus, the concepts of quasi-equilibrium state involved in the DLA and cluster models of the structure of amorphous polymers are similar in physical essence, the quantitative estimations in terms of these two models providing consistent results. The

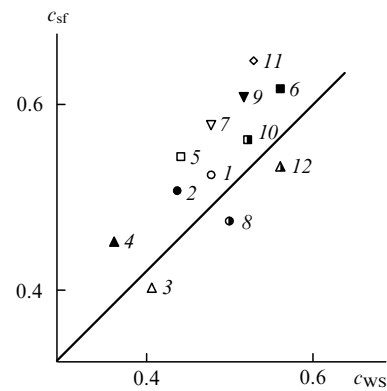


Figure 40. Relationship between the concentrations of free particles c_{WS} and statistical segments in the loosely packed matrix c_{sf} for the quasi-equilibrium state;

(1) polyethylene, (2) poly(methyl methacrylate), (3) polystyrene, (4) polytetrafluoroethylene, (5) polypropylene, (6) polycarbonate, (7) poly(ethylene terephthalate), (8) poly(vinyl acetate), (9) poly(ethylene oxide), (10) polycaprolactam, (11) polyestersulfone, (12) poly(vinyl chloride).

macromolecular ‘loops’, which restrict the mobility of polymer chains act as the ‘seeds’ in the WS model.¹⁷⁸

3. Order and fractality in polymers

The temperature dependences of V_{cl} for different polymers are similar. Raising the temperature results in a decrease in V_{cl} , the rate of thermofluctuational decomposition of clusters sharply increasing as T approaches T_g (or T_m). This general regularity is illustrated by the plots for V_{cl} vs. testing temperature for polycarbonate, poly(methyl methacrylate) and high-density polyethylene (Fig. 41). Note that similar temperature dependences are obeyed by the mechanical properties of polymers (elastic modulus, yield point, *etc.*).¹⁹¹ This similarity implies the possibility of superposition of the $V_{cl}(T)$ curves for different polymers, which is due to the common pattern of variation of the degree of local ordering vs. temperature. Below we construct this superposition and consider some its consequences in terms of the cluster model resorting to percolation theory and fractal analysis.⁶⁰

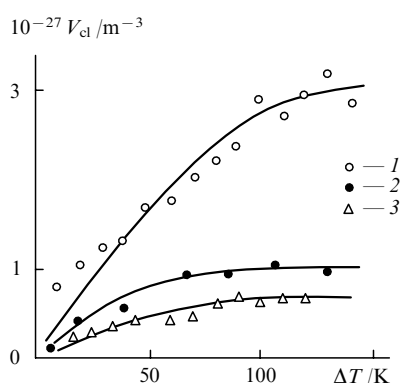


Figure 41. Density of the cluster network of entanglements V_{cl} vs. reduced testing temperature $\Delta T = T_g - T$ for polycarbonate (1), poly(methyl methacrylate) (2) and $\Delta T = T_m - T$ for high-density polyethylene (3).⁶⁰

The dependences of V_{cl} on the reduced temperature $\Delta T = T_g - T$ for some polymers follow similar patterns (see Ref. 41); therefore, a scaling relation of the following type can be applied:

$$V_{cl} \propto \Delta T^x, \quad (104)$$

where x is a generalised index.

However, the degree of local ordering is reflected more precisely by the relative portion of clusters φ_{cl} , determined from Eqn (53). An obvious advantage of Eqn (53) is the fact that it includes the main molecular characteristics of polymers. Figure 42 shows the $\ln \varphi_{cl}(\ln \Delta T)$ plots for the three polymers mentioned above and for the epoxy polymer EP-1, which are approximated by a common straight line. It can be easily seen that

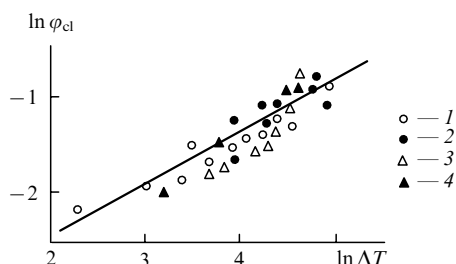


Figure 42. Relative portion of the clusters φ_{cl} vs. reduced testing temperature ΔT for polycarbonate (1), poly(methyl methacrylate) (2), high-density polyethylene (3) and EP-1 (4).⁶⁰

these data comply well with the known relation of percolation models in the case of critical transition¹⁶²

$$P_\infty \propto (T_g - T)^\beta. \quad (105)$$

In this interpretation, the φ_{cl} value corresponds to the ‘power’ of an infinite cluster, *i.e.* the probability P_∞ that a unit belongs to the infinite cluster. Thus, at T_g (or T_m), the cluster network of entanglements appears (or vanishes); simultaneously, the structure of a vitreous polymer sample as a system is formed (or destroyed). Several other important points related to the possibility of describing a polymer structure in terms of Eqn (105) deserve attention. In the cluster model, the statistical segment l_{st} is taken as the ‘section of rigidity’ of a chain. The l_{st} value is several times smaller than the Kuhn segment length A , which characterises the rigidity of a freely jointed chain.⁹¹ When the A value is chosen as the ‘section of rigidity’, the φ_{cl} values prove to be greater than unity in most cases, which is devoid of physical meaning. The relationship between A and l_{st} can be written in the following form:

$$l_{st} = A \cos \frac{\theta_v}{2}, \quad (106)$$

where θ_v is the bond angle.

Thus, the shorter length of the chain section of rigidity l_{st} in the vitreous state is due to the conformational rearrangements peculiar to this state.

In the case of amorphous-crystalline high-density polyethylene, the reduced φ'_{cl} value was used; this parameter characterises φ_{cl} with respect to the whole polymer bulk rather than to the amorphous phase alone

$$\varphi'_{cl} = \frac{\varphi_{cl}}{1 - k}, \quad (107)$$

where k is the degree of crystallinity.

The relation modified for the case of amorphous-crystalline polymers is represented by Eqn (53). Using Eqns (53) and (23), one can elucidate the relationship between d_f and φ_{cl}

$$d_f = d - 5.98 \times 10^{-10} \left(\frac{\varphi_{cl}}{C_\infty S} \right)^{1/2}, \quad (108)$$

where S is expressed in $\text{\AA}^2$.

As has been shown above, Eqn (45) provides the minimum values for the fractal dimension of structure ($d_f^\dagger$) possible for a given polymer, which are in good agreement with the d_f^0 values (see Table 1). Hence, by substituting $d_f^\dagger$ or d_f^0 into Eqn (108), one can estimate the limiting degree of local ordering (φ_{cl}^0) possible for a given polymer as a function of the most important molecular characteristics of the polymer, C_∞ and S . When the temperature decreases below T_0 (at which the φ_{cl}^0 value is attained), the degree of local ordering does not change; therefore, T_0 can be regarded as an analogue of the temperature T_∞ at which the polymer reaches a constant free volume.^{106, 173, 191, 192} Meanwhile, T_0 can be found from Eqn (104) provided that $\varphi_{cl} = \varphi_{cl}^0$. The T_0 and T_∞ values thus obtained, together with the temperatures of transition to a state with a constant value of density fluctuations T^* ,^{106, 193} for eight polymers are listed in Table 3. It can be seen that T_0 and T_∞ are in good agreement for all polymers except polycarbonate, for which the calculation gave $\Delta T = 670$ K, which has no physical meaning. For real polymers, the tendency towards a thermodynamically more equilibrium state should be counterbalanced at a certain point by the force of chain ‘tightening.’ Therefore, the value $d_f = 2.5$ should be used instead of $d_f^\dagger$. In addition, the value $\varphi_{lp} = 1$ (*i.e.* $\varphi_{cl} = 0$) is attained at $d_f = 2.92$ rather than at $d_f = 3$, as could be suggested in view of Eqn (108). With allowance for these corrections, calculation in terms of Eqn (105) affords $T_0 \approx 318$ K for polycarbonate, which is consistent with the value $T_\infty = 323$ K (see Table 3). The correspondence between T_0 and T^* is poorer than that between T_0 and T_∞ but the patterns of their variation for polymers fully coincide.

Table 3. Temperatures of the transitions to the 'frozen' free volume T_∞ , quasi-equilibrium state T_0 and a constant density fluctuation T^* .

Polymer	T_∞ / K	T_0 / K	T^* / K
Poly(ethylene terephthalate)	280	300	220–250
Polyamide-6	277	304	200
Polyethylene	227	243	140–150
Polypropylene	227	199	210
Polystyrene	324	320	270
Poly(methyl methacrylate)	290	269	250–280
Poly(vinyl chloride)	270	333	220
Polycarbonate	323	318	200–220

The following empirical relation between the change in the specific Gibbs function of the formation of the supermolecular structure ΔG during the self-assembly of the cluster structure and φ_{cl} has been derived¹⁹⁴

$$\Delta G \propto \varphi_{cl}. \quad (109)$$

Substitution of this relation into Eqn (108) gave the expression

$$\Delta G \propto C_\infty S(3 - d_f)^2. \quad (110)$$

The ΔG value for the supercooled liquid–solid nonequilibrium phase transition has been reported.¹⁹⁵ It follows from relation (110) that $\Delta G = 0$ when $d_f = 3$, *i.e.* when the fractal properties are lost. In other words, the fact that fractal structures are formed only in nonequilibrium processes has been confirmed once again.¹²

4. The possibility of numerical modelling of polymer properties

Little is known about a polymer synthesised from monomers or prepared by curing an oligomer; as a rule, the known data include the trademarks of monomers, oligomers, and curing agents and their ratios. Evidently, in this situation, for example, in the case of network polymers, the main initial parameter — cross-linking density v_s — can be either calculated¹⁵⁴ or determined experimentally.¹⁹² In the latter case, the molecular mass of the chain section between the cross-linking points M_s is calculated using the equation

$$\frac{1}{M_s} = \frac{F_i m}{2W}, \quad (111)$$

where F_i is the functionality of the curing agent, m is the number of moles of the curing agent in the sample, and W is the sample weight.

Comparison of the $T_g(v_s)$ plots for different epoxy polymers for which the v_s values were determined by both methods mentioned above shows that the experimental values are somewhat lower than the calculated ones. This discrepancy can be eliminated by introducing the correction factor C . The discrepancy is due to two reasons; one reason is the use of different batches of epoxy resins and curing agents and the other reason is that the calculation implies completeness of the curing reaction, *i.e.* that the curing agent has been entirely consumed, which does not occur in reality.

Apart from v_s , it is necessary to estimate the cross-section area of the macromolecule S and the length of a real bond in the backbone l_0 . The S value is either taken from reference data (if they do exist) or estimated by comparison with the S value of a linear polymer with a similar chemical structure. For example, the chemical structures of the epoxy resins and polycarbonate are similar because they both are based on bisphenol A. Therefore, the value $S = 0.31 \text{ nm}^2$, determined for polycarbonates, was used for these epoxy polymers.⁷⁶ Experimental estimates have shown⁷¹ that this approximation is correct to within $\sim 5\%$. As regards the l_0 value, it characterises a class of polymers rather than a

particular polymer, which makes its determination easier. Since epoxy resins are heterochain polymers, $l_0 = 0.125 \text{ nm}$.⁷⁶

Using the above parameters, one can estimate the length of the section of a macromolecule between chemical cross-linking points and the distance between chemical cross-linking points.¹⁴ The subsequent stage is to solve a set of three equations with three variables, namely, the characteristic ratio C_∞ and the fractal dimensions of the macromolecule section between chemical cross-linking points D and of the cluster structure d_f . By solving this set of equations, one can find these structural characteristics of the epoxy polymers. After that, the Poisson coefficient should be found from Eqn (23) and the cluster network density V_{cl} should be determined from the relation

$$\mu = 0.5 - 2.98 \times 10^{-10} (V_{cl} l_0)^{1/2}. \quad (112)$$

Finally, the relative portion of clusters is calculated as

$$\varphi_{cl} = \frac{V_{cl}}{V} \quad (113)$$

where V is the polymer volume.

For the loosely packed matrix,⁶⁰

$$\varphi_{lp} = 1 - \varphi_{cl}. \quad (114)$$

Thus, we have obtained a complete set of characteristics of the molecular, topological, and supermolecular levels of the structure of cross-linked polymers, which permits one to model and predict their properties. The properties chosen include three characteristics for applications (elastic modulus E , yield point σ_p and glass transition temperature T_g), which are needed to develop new materials, and three characteristics which are regarded conventionally as theoretical (Grüneisen parameter γ , thermal expansion coefficient α_t and yield strain ϵ).

It should be taken into account that one order parameter (for example, φ_{cl}) is inadequate to describe the structure and properties of an amorphous polymer. It has been shown in relation to linear polymers¹⁹⁶ that the need for a second order parameter is due to the thermodynamic nonequilibrium of the loosely packed matrix. In other words, $f_{iv} \neq f'_{iv}$. Therefore, a second order parameter was introduced for linear polymers, namely, $(f'_{iv} - f_{iv})/f_{iv}$. In the case of cross-linked polymers, the constant contribution to f_{iv} caused by the presence of chemical cross-linking points should be additionally taken into account as f_{iv}^* ($f_{iv}^* = 0.024$, see Refs 70, 185). The use of percolation models¹⁹⁷ results in the relation

$$G \propto \left(\varphi_{cl} - \frac{f'_{iv} - f_{iv}^* - f_{iv}}{f_{iv}} \right)^A, \quad (115)$$

where G is the shear modulus, $A \simeq 1.5$.

Having determined f'_{iv} from relation (70) and f_{iv} from relation (55), one can find the shear modulus and then, using Eqn (44), the elastic modulus.

The relation for determining the yield point derived using relations (23) and (44) has the form

$$\sigma_p = \frac{E(3 - d_f)}{3d_f}. \quad (116)$$

The σ_p value can also be estimated using the equation^{198, 199}

$$\sigma_p = \frac{3^{1/2} G b (l_{st} V_{cl})^{1/2}}{2\pi}, \quad (117)$$

where b is the Burgers vector, determined from the empirical relation¹²⁹

$$b = \left(\frac{52.2}{C_\infty} \right)^{1/2}. \quad (118)$$

The glass transition temperature T_g can be found either using an empirical equation⁷¹ or in terms of the fractal approach to glass transition. This is done either using a general model or a

model which takes into account the stabilising influence of chemical cross-links *via* the factor $v_s^{1/2}$ (see Ref. 200).

The Grüneisen parameter γ can be determined by one of the following methods: calculation in terms of relation (69) using the parameter D_f (equal to D_{fv}), determined previously from Eqn (39); calculation in terms of Eqn (68); or calculation using the relation

$$\gamma = \frac{9\pi^2}{4(S^{1/2} + l_0)(l_{st} V_{cl})^{1/2}} - 0.25. \quad (119)$$

The thermal expansion coefficient a_t can be found from the equation

$$\gamma = \frac{3 + a_t T(3 + a_t T)}{6a_t}. \quad (120)$$

The yield strain ε is found from relation (67) provided that $\varepsilon = \varepsilon_c$.

Thus, the approach making use of the cluster model of the structure of amorphous polymers and fractal analysis provides the possibility of numerical modelling of the structures and properties of network polymers. An obvious advantage of this procedure is the fact that only v_s and S are actually used as calculation parameters. It should be noted that the simplicity of choosing the input data is combined with the strict physical interpretation of these data and, hence, no empirical adjusting coefficients are required.

IV. Experimental determination of the fractal dimension

1. A brief survey of the methods

Various methods are used to determine the fractal dimension,^{61, 201} which can be conventionally divided into two groups: fractographical and physical methods, based on the relationship between the fractal dimension and physical properties. The former group includes the methods of horizontal sections (cut islets),^{202–207} vertical sections,^{13, 208–211} profile Fourier analysis,^{203, 212} decantation, expansion, and cell counting,^{61, 213} similarity transformation,^{214, 215} *etc.* The fractographic methods used to gain fractal information on the irregularity of fractured surfaces make it possible to investigate profiles as horizontal or vertical sections of the surface. This requires additional hypotheses to attain reliability of the relationships between the surface fractal properties and size.^{208, 216, 217}

The main goal of fractographic measurements is to determine the fractal dimension of, for example, chipped (fractured) surface and the limits in which the surface exhibits fractal properties. The main problem is the legitimacy of measuring the fractal dimension of self-affine fractured surfaces. The horizontal profile of a fractured surface can be statistically self-similar but the vertical profile is usually self-affine.^{218, 219} Thus, the horizontal and vertical surface sections have absolutely different scaling characteristics, which need to be estimated using different procedures of measurements.

In the case of statistically self-similar horizontal contours, any sensible procedure for determination of the fractal dimension should give the same value.⁸⁷ The question is how this fractal dimension is correlated with the fractal properties of the self-affine fractured surface. Self-affine vertical profiles can be characterised by many fractal dimensions, for example, local and global fractal dimensions. The latter are always equal to the topological dimension of the profile, while the local dimensions of the profile irregularities can be represented as exponential functions.²²⁰

The second group of methods comprises various physical methods used most often for fractal analysis of surfaces (mainly, fractured surfaces). They include porometry,^{211, 222} scattering procedures (*e.g.*, small-angle neutron scattering),¹³ optical diffraction methods,^{13, 61, 182, 223} secondary electron emission measurement,¹³ adsorption–desorption measurements (adsorption

probe method),^{13, 224–227} methods of thermodynamics,²²⁸ the deposit experiment method,²²⁹ electro- and thermochemical methods,^{229, 230} NMR measurements of the pore distribution,²³¹ procedures based on the results of mechanical measurements,^{61, 232} *etc.*[§]

2. Small-angle X-ray diffraction

As an example, we shall consider the practical application of one method, small-angle X-ray scattering (SAXS), which is widely used to study the fractal structure of solids.^{227, 233–245} Polymers are mainly studied by this method during cross-linking in solutions.^{233–235} The theoretical grounds of the method have been developed fairly well by now.^{238, 241, 242} The fractal structures of block polystyrene, poly(methyl methacrylate), and polycarbonate have been studied by the SAXS method.¹⁵³ These particular polymers were chosen because they are often used as model systems and, therefore, they are well characterised and because the structures of macromolecules⁷⁶ and, as a consequence, the properties of these polymers are different.²⁴⁴

The use of the SAXS method is based on the characteristic power dependence of the scattering intensity I on the scattering vector

$$I(k) \propto k^{-x}, \quad (121)$$

where x is a Porod index, the interpretation of which depends on the nature of the scattering source

$$k = 4\pi\lambda^{-1} \sin \frac{\theta}{2}, \quad (122)$$

where λ is the X-ray radiation wavelength and θ is the scattering angle.²²⁴

In the case of bulk fractals (*i.e.* structures like polymers), this index coincides with the fractal dimension of the structure d_f .^{224, 242}

For a fractal phase interface with the dimension D_i , the following relation holds:²³⁸

$$I(k) \propto k^{D_i-6}, \quad 2 < D_i < 6. \quad (123)$$

Figure 43 shows the $\ln I(k)$ plots, while Fig. 44 presents the dependences of $\ln I$ on k^2 for the polymers mentioned above.²⁴⁵ Two linear sections present for each polymer of Fig. 43 point to the existence of two regions with different fractal dimensions. These plots differ from the analogous plots for silicates, for which the slope of the $\ln I(k)$ plots increases discretely with an increase in k (which implies the loss of fractal properties), but are similar to the dependences obtained for amorphous chalcogenide films.²⁴² To identify the structural regions responsible for the observed change in the slope, the cluster model for the structure of

§ Experimental methods for determining the fractal dimension are considered in detail, for example, in a monograph.²³⁷

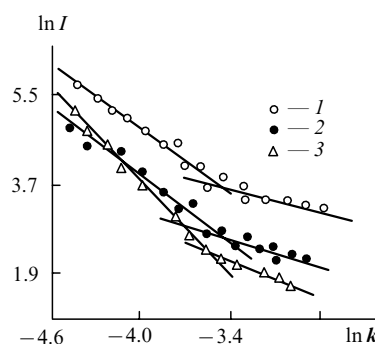


Figure 43. SAXS intensity *vs.* scattering vector k for poly(methyl methacrylate) (1), polystyrene (2), polycarbonate (3).³⁹

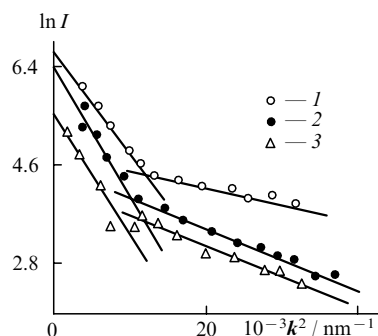


Figure 44. SAXS intensity vs. k^2 for poly(methyl methacrylate) (1), polystyrene (2), polycarbonate (3).³⁹

amorphous polymers was used. The region of local order and the sections of macromolecules protruding from it should be considered as the fractal cluster.¹²⁵ The size of this cluster is twice the distance between the regions of local order, and its fractal dimension characterises the structure of the whole polymer, which is a set of generalised fractal clusters. Another structural region is represented by the loosely packed matrix located between the local order regions; all the fluctuation free volume is accumulated in this region. The R_{cl} values for the polymers considered are listed in Table 4. Using the plots presented in Fig. 44 one can calculate the Guinier radii.²⁴⁵ Attention is drawn by the facts that R_G and R_{cl} are close in magnitude and that R_G increases twofold on passing from one linear section to the other (Fig. 43), which corresponds to the transition from R_{cl} to $2R_{cl}$. This suggests that the R_G and R_{cl} values reflect the same structural parameter. The condition for the fractality of particles which scatter X-rays in the range of small angles is known²²⁴ to be represented by the inequality $R_G k \geq 1$.

Table 4. Structural and fractal characteristics of amorphous polymers.

Polymer	R_{Cl}/nm		$d_{\text{fp}} \quad D_{\text{fp}} \quad d_{\text{f}} \quad D_{\text{f}}$				
	$k < 0.028^{-1} \quad k > 0.028^{-1}$						
Polystyrene	4.1	10.0	5.0	2.80	5.12	2.75	5.0
Poly(methyl methacrylate)	3.7	10.0	5.0	2.80	5.20	2.70	4.33
Polycarbonate	3.0	8.0	4.0	2.40	4.40	2.62	3.63

The presence of two R_G values implies the existence of a boundary between fractal structural regions, which can be found from the condition $R_G k \geq 1$. For a fractal cluster with the size $2R_{cl} \approx 7.0$ nm, this corresponds to $k \approx 0.00143$ nm⁻¹ or $\ln k \approx 4.25$, which is the upper limit of fractality of the polymer structure. When $R_G \approx R_{cl} \approx 3.5$ nm, we have $\ln k \approx -3.56$, which is consistent with the $\ln k$ value at which the slope of the plots in Fig. 43 changes.

Thus, the section of the dependence of $\ln I$ on $\ln k$ for $\ln k$ ranging from 4.25 to -3.56 can be associated with the cluster structure of an amorphous polymer and the section for $\ln k > -3.56$ is matched by the loosely packed matrix.

The existence of these boundaries is due to a known feature of real fractals — the fractal behaviour is realised only within a definite scale range. Several ranges have been determined for amorphous solids;²⁴² we shall distinguish two of them which correspond to the k values used. If the size of a cluster of pores[¶] is designated by η_p and the size of a pore is designated by a_p , the

¶ In amorphous polymers, the term ‘pores’ is used in relation to microcavities of free volume and the term ‘cluster of pores’ refers to the loosely packed matrix in which they are concentrated.

dimension of structural elements will be estimated in the following ranges of k . When $k < \eta_p^{-1}$, the dimension of the structure itself is determined, while for $\eta_p^{-1} < k < a_p$, the dimension of the cluster of pores is found. It has been shown¹⁸⁹ that the fluctuation free volume in a polymer is a fractal object, its dimension being equal to the dimension of the regions of localisation of excess energy D_f .²⁴⁶ In other words, D_f characterises the degree of energy excitation of the loosely packed matrix. The dimensions d_f and D_f can be found from relations (23) and (39), respectively.

The d_{fp} values estimated from Eqn (123) with allowance for the slope of the plots shown in Fig. 43 ($\ln k$ is -4.25 to -3.56) are summarised in Table 4. The d_f values found using Eqn (23) are given for comparison. The fact that the values thus obtained are close confirms the validity of this interpretation.

The slope of the plot sections for $\ln k > -3.56$ is close to unity; it cannot be interpreted as the fractal dimension of a structural element if for no other reason than its magnitude. Therefore, Eqn (123) was used to determine the fractal dimension. Comparison of the D_{fp} and D_f values obtained in this way [see Eqn (39)] showed that they are in good agreement (see Table 4). Note that a slope of the order of unity (-0.75 to -0.80) has also been obtained for a similar k range for amorphous chalcogenide films; however, this result was not interpreted.²⁴²

The condition $R_G k \geq 1$ is usually obeyed for larger angles in the small-angle region. However, in the case of relatively large structural elements, the region of fractality and the Guinier region can overlap. Apparently, this overlap also takes place for the polymers under consideration. The range of linearity of the plots shown in Figs 43 and 44 is $(1-3) \times 10^3$ nm⁻¹ and $R_G \approx 10$ nm, i.e. the product $R_G k$ falls in the range from 1 to 3. The overlap of the fractality and Guinier regions may imply a relationship between the fractal dimension d_f and the Guinier radius R_G . This can be demonstrated analytically in the following way. According to the small-angle Guinier approximation, the following relation holds:²⁴⁵

$$I = I_0 \ln \left(-\frac{R_G^2 k^2}{3} \right), \quad (124)$$

while in the range of the Porod large angles, the relation¹⁵³

$$I = C k^{-d_f}, \quad (125)$$

is valid, where I_0 and C are constants. For equal I , there exists a formal relationship between d_f and R_G ¹⁵³

$$d_f = \frac{(R_G^2/3)k - \ln(I_0/C)}{\ln k}. \quad (126)$$

It is noteworthy that this relationship is not obligatory in terms of the cluster model. An increase in R_G means an increase in the distance between the clusters, a decrease in V_{cl} , an increase in μ , and the corresponding increase in d_f , which is reflected by relation (126).

We would like to note yet another important aspect of determination of d_f by the SAXS method. Based on the data of previous publications,^{238, 246} Novikov *et al.*^{167, 182} estimated the d_f values for amorphous vitreous polymers to be 2.0–2.2. In another study,²⁴⁷ polystyrene has been tested at 16 K; as shown above, transfer of this result to the temperature range of about 293 K is improper. Studies of the silicate colloid aggregates^{224, 241, 248} showed that their porosity influences appreciably the d_f value. Thus pressing (i.e. an increase in the density) of samples results in markedly higher d_f ranging from 2.55 to 2.65.²⁴¹ Feder¹³ obtained $d_f = 2.56$ for protein aggregates. These results are in good agreement with the data obtained in terms of Eqn (23) and with the above SAXS data. Therefore, any estimates assuming *a priori*, without sufficient grounds, $d_f \approx 2$ for amorphous vitreous polymers can induce substantial errors, for example, in the calculation of d_s .^{167, 182}

Thus, the SAXS methods make it possible to confirm the fractality of different structural components of amorphous vitreous polymers and to measure their fractal dimensions. The upper limit of the fractal behaviour of polymers, equal to $\sim 2R_{cl}$, is also in good agreement with the estimate of this value reported by Novikov *et al.*¹⁶⁷

V. Conclusion

A feature distinguishing the fractal approach from the physical models of polymer synthesis developed previously is that it takes into account the structure of the macromolecular coil, which determines the polymer structure, and characterises simultaneously the fractal dimension of the coil and the particular mechanism of the coil formation. The results obtained along this line indicate that the growth of macromolecules during the polymer structure formation stops when the macromolecular coil has reached the density of the reaction medium rather than due to exhaustion of the chemical reactants, *i.e.* the reaction is terminated by purely physical factors. This conclusion is impossible in terms of the Euclidean geometry.

Based on fundamental physical principles, the multilevel polymer structure has been described and the equations relating the molecular characteristics, topology, and parameters of the supermolecular structure of polymers are analysed. The application of principles of nonequilibrium thermodynamics and treatment of vitreous polymers as structurally inhomogeneous solids provided understanding of the fact that the mechanical energy applied during deformation is 'pumped' into the loosely packed regions of the polymer and dissipated in the closely packed regions (clusters). The dissipation of mechanical energy induces shear stress in the clusters; the clusters lose their stability, which causes the polymer to yield.

Analysis of the concept of the fluctuation free volume in a vitreous polymer has shown that it possesses fractal properties; hence, the microcavities composing this volume can be modelled by a D_{fr} -dimensional sphere. The microcavity size is restricted by the volume in which the energy of thermal fluctuations needed for their formation is accumulated. It is shown that 'stretching' of macromolecules hampers an increase in the degree of ordering. When the thermodynamic forces inducing these effects are counterbalanced, the polymer reaches a certain quasi-equilibrium state, which is explained by a density fluctuation above a particular temperature below the glass transition temperature. The introduction of the concept of the quasi-equilibrium state of polymers provides a better understanding of several experimental findings.

The results of modelling the polymer structure using percolation and aggregation theory showed that the structure formed at the glass transition temperature is a percolation cluster. Glass transition is assumed to be a phase transition. The fractal dimension of these structures is determined by the disorder generated by deterministic chaos. Simultaneously, it was shown that the polymer structure can be modelled by a modified model of the diffusion-limited irreversible aggregation. The superposition of the cluster volume-temperature curves for amorphous and amorphous-crystalline polymers and the relationship between fractality and local order in the structure of vitreous polymers were described within the framework of the cluster model resorting to the percolation theory. The importance of calculation of the properties of polymers is demonstrated by presenting a procedure based on the cluster model of the amorphous state structure and fractal analysis. This procedure allows one to perform numerical modelling of properties of, for example, cross-linked polymers. An obvious advantage of this method is the simplicity of choosing the input data in combination with strict physical interpretation and the absence of adjusting coefficients.

This brief survey of the methods of determination of the fractal dimension and the practical application of the SAXS procedure for determining the fractal dimension demonstrates

the prospects for using the fractal approach for the investigation of the structure and properties of polymers.

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^b — *Polym. Sci. (Engl. Transl.)*

^c — *Inorg. Mater. (Engl. Transl.)*

^d — *Russ. J. Phys. Chem. (Engl. Transl.)*

^e — *Physics-Uspekhi (Engl. Transl.)*

Phase relations in ternary oxide systems of Group III and VB elements in a subsolidus region. Ternary oxide compounds

M G Zuev

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Abstract. Phase relations in the subsolidus region are considered for 54 ternary systems including $M_2O_3-V_2O_5-R_2O_5$, $Y_2O_3(La_2O_3, Sc_2O_3)-Nb_2O_5-Ta_2O_5$, $M_2O_3-B_2O_3-R_2O_5$, $M_2O_3-Ga_2O_3-R_2O_5$, $Al_2O_3-V_2O_5-R_2O_5$ (where M is a rare-earth element and $R = \text{Ta, Nb}$). The criteria determining the formation of ternary oxide compounds were found to include the cation sizes and the ratios between the radii of the ions constituting the anionic part of the compounds. The crystal-chemical characteristics are presented for MR_2VO_9 , $LaRB_2O_7$, La_4VBO_{10} , Ln_7VBO_{17} ($Ln = \text{La, Pr, Nd}$), $La_3Ga_{5.5}R_{0.5}O_{14}$. The vibrational spectra of polycrystals of ternary compounds and solid solutions based on them are described in detail. The bibliography includes 154 references.

I. Introduction

One of the primary tasks of chemistry is the development and creation of new materials. Simple and complex oxides have found very wide use in many branches of industry. Synthesis of new materials based on complex oxides and the improvement of existing technologies for the production of these materials are based both on the study of the phase diagrams of oxide systems and on fundamental investigations into the 'composition-structure-properties' relationships.

Owing to the vast diversity of their properties, complex oxides of V, Ta, Nb and elements of the Group III of the Periodic Table are of special interest. For example, oxide crystals of Group III and VB elements are used as photo-, cathodo- and X-ray active luminophores. A topical task is the search for medical and luminescent materials that possess new spectroscopic parameters which might be expected among compounds of transition elements.

For instance, efficient tantalum-based X-ray active luminophores have acquired ever growing importance in recent years.^{1–3} They possess higher specific density $[(7.5–9.7) \times 10^3 \text{ kg m}^{-3}]$ than other X-ray active luminophores used in common practice and a number of other advantages allowing the production of intensifying X-ray screens with higher resolution and speed. This

makes it possible to decrease significantly the radiation dose that affects the patients during X-ray examinations, a feature especially important for X-ray diagnostics of children.

Rare-earth element (REE) tantalates are crystals which efficiently absorb X-ray radiation with a quantum energy from 10 to 150 keV and are widely used in medicine. Complex tantalum-containing REE oxides are used as novel X-ray contrast agents (RCA) that are precipitated on body tissues and absorb X-ray radiation. This enhances contrast, which allows one to perform more accurate diagnostics at lower irradiation doses absorbed by the patient.^{4–8} The physicochemical properties of these compounds have not been studied sufficiently yet. Studies of the phase diagrams of complex oxides and their solid solutions used as RCA will aid in filling this gap.

Compounds of the general formula MR_2VO_9 exist in ternary systems $M_2O_3-V_2O_5-R_2O_5$ ($M = \text{REE}$; $R = \text{Nb, Ta}$).⁹ Based on these compounds, a new type of complex-oxide phosphor crystal has been developed. Synthesis of these compounds is accompanied by spontaneous formation of optical centres VO_4^{4-} owing to which the crystals of MR_2VO_9 possess narrow-band luminescence, predominantly in the red region of the spectrum. These phosphor crystals have an unusual temperature dependence of irradiation: the intensity of red luminescence of the centres increases on heating, whereas that of the support is quenched.¹⁰ This effect contradicts the law of thermal luminescence quenching and has not been rationalised yet.

A physicochemical substantiation of the properties of complex oxides listed above requires primarily a detailed study of the regularities of their formation by considering phase relations in ternary systems. The types of phase diagram often vary for REE-containing systems:¹¹ purely eutectic systems exist in equilibrium with chemical compounds. In addition, one or several compounds can exist only for some of the elements rather than for the entire REE series. As a result, isostoichiometric series are formed which are grouped in complete or incomplete morphotropic and isostructural series. The change in the type of phase diagrams of ternary systems depending on the nature of the REE is shown below.

The purpose of this review is to generalise data on the phase relations in ternary[†] oxide systems of Group III and VB elements

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[†] The phase composition of restriction-type binary systems, viz., $M_2O_3-R_2O_5$ ($M = \text{B, Al, La, Y, Sc, Ln}$; $R = \text{Ta, Nb, V}$), $M_2O_3-B_2O_3$ ($M = \text{La, Y, Sc, Ln}$), $La_2O_3-Ga_2O_3$, $V_2O_5-R_2O_5$ ($R = \text{Ta, Nb}$), $Ta_2O_5-Nb_2O_5$, as well as the chemistry of the compounds formed from them have been described in detail elsewhere.^{12–82}

in a subsolidus region, to reveal the regularities of the formation of ternary oxide systems and to analyse their vibration spectra. The vibration spectra not only provide information on the structure of the crystal lattices of ternary compounds but also make it possible to predict the luminescent properties of phosphor crystals. Based on the analysis of vibration spectra with the use of the concept of elementary lattice excitations (phonons), one can make conclusions on the filling of the energy gaps between the excited states of optical centres and describe the processes responsible for the excitation energy transfer in phosphor crystals.

II. Phase relations in $M_2O_3 - V_2O_5 - Ta_2O_5$ systems ($M = \text{REE}$)

Figure 1[†] shows phase relations in tantalum-containing $M_2O_3 - V_2O_5 - Ta_2O_5$ systems in a subsolidus region up to 1200 °C.^{83–98} For each REE, ternary oxides with the composition MTa_2VO_9 (henceforth referred to as vanadatotantalates) were found in these systems. When a mixture of the starting compounds is heated, thermodynamic equilibrium is established faster the higher the temperature. Under isothermal sintering conditions at temperatures > 1100 °C, the $M_2O_3 - V_2O_5$ systems are equilibrated in 6–8 h, while the $M_2O_3 - Ta_2O_5$ systems require 30–70 h (for comparison: the equilibrium in the $M_2O_3 - Ta_2O_5$ system at 900 °C is established in > 100 h). It takes more than 10 h to equilibrate the $V_2O_5 - Ta_2O_5$ system.^{18,44} Equilibration of the ternary systems $M_2O_3 - V_2O_5 - Ta_2O_5$ takes approximately the same time as that of the $M_2O_3 - Ta_2O_5$ systems.⁹ Vanadatotantalates decompose above 1200 °C to give the corresponding REE metatantalates and an unknown phase.⁸⁶ In a subsolidus region, all compounds of the ternary system are stable. The difference in triangulation depends only on the existence of certain binary compounds in the $M_2O_3 - V_2O_5$ (up to 50 mol. % M_2O_3) and $M_2O_3 - Ta_2O_5$ systems (50 mol. %–100 mol. % Ta_2O_5).

According to the data of laser radiation second harmonics generation (SHG) measurements, ternary oxides of scandium and cerium subgroup elements can be assigned centrosymmetrical crystals.⁹ X-Ray diffraction data⁹ suggest that the structures of MTa_2VO_9 ($M = \text{La, Y, Pr, Nd, Sm, Eu}$) are close to those of the corresponding tantalates MTa_7O_{19} which possess hexagonal symmetry. For this reason, solid solutions can be formed in the $MTa_2VO_9 - MTa_7O_{19}$ system. Table 1 lists the unit cell parameters for MTa_2VO_9 crystals. It should be noted that YTa_2VO_9 has two crystal modifications conventionally designated as α and β . The α modification is structurally similar to $LaTa_2VO_9$, while the β modification is similar to $ScTa_2VO_9$.

Table 1. Unit cell parameters of hexagonal crystals of MTa_2VO_9 .

M	a^a /nm	c^a /nm	V /nm ³
La	0.6231	1.9573	0.658
Ce	0.6152	0.9932	0.653
Pr	0.6124	1.9831	0.643
Nd	0.6143	1.9864	0.648
Sm	0.6192	1.9723	0.654
Eu	0.6121	1.9812	0.643
Y ^b	0.6189	1.9831	0.655

^a The error of determination is ± 0.0005 nm. ^b The α - YTa_2VO_9 phase.

ters for MTa_2VO_9 crystals. It should be noted that YTa_2VO_9 has two crystal modifications conventionally designated as α and β . The α modification is structurally similar to $LaTa_2VO_9$, while the β modification is similar to $ScTa_2VO_9$.

The structures of vanadatotantalates of scandium and yttrium subgroup elements differ from those of compounds of cerium subgroup elements. The structure of MTa_2VO_9 crystals has not been determined yet.

One can see from Table 1 that the parameters a and c and the unit cell volumes of vanadatotantalates do not depend linearly on the lanthanide ionic radii, as opposed to simple tantalates⁹⁹ and mixed-cation compounds.¹⁰⁰ It is believed⁹⁹ that the decrease in the unit cell parameters of tantalates with the decrease in the REE ionic radii can be explained by a decrease in the degree of covalence of the M–O bond, which changes essentially along the series from scandium to yttrium, lanthanum and from cerium to lutetium. Evidently, other factors are important in the case of vanadatotantalates.

It is well known that REE compounds display periodicity of structural and structure-dependent properties. These properties change non-monotonically for several reasons; the major of these include the energetic and spatial deepening of orbitals, the alteration of the type of exchange interactions between unpaired electrons, spin-orbital stabilisation, the nephelauxetic effect and the stabilising effect of the crystal field.¹¹

Table 1 shows that praseodymium and europium vanadatotantalates have the smallest parameters a and unit cell volumes. Hence, it can be assumed that an additional decrease in the energy of the $4f$ orbitals occurs in $PrTa_2VO_9$ and $EuTa_2VO_9$ due to spin-orbital interaction. This affects the contribution of the f orbitals to the formation of chemical bonds and probably the shape of the coordination polyhedra of these compounds. It is noteworthy that there is a small ‘gadolinium’ inflexion of a values for $LnTa_7O_{19}$ crystals ($Ln = \text{Ce} - \text{Lu}$).¹⁰¹

No sharp changes in the X-ray diffraction parameters are observed in the series $LnTa_2VO_9$ ($Ln = \text{Gd} - \text{Lu}$). These crystals are isostructural, which is corroborated by the data from vibrational spectra (see Section VI).

Some crystal-chemical features of vanadatotantalates were established using NMR spectroscopy.⁸³ In particular, the type of coordination polyhedra formed by oxygen around the vanadium ions was determined. The spectra were assigned using NMR data for known compounds.^{102–106} The spectra for a sample of YTa_2VO_9 were recorded at frequencies of 105.2 and 78.86 MHz without and with magic-angle spinning (MAS). The spectrum consisted of a single line. The magic-angle spinning enabled fairly accurate determination of the isotropic shift. The MAS spectra recorded at two operating frequencies of the spectrometer display quadrupole splitting of the central transition. Figure 2 (curve 1) shows a ⁵¹V NMR spectrum for YTa_2VO_9 measured at 78.86 MHz without consideration of the quadrupole correction $\delta_{\text{iso}} = -665 \pm 2$. The small anisotropy of the chemical shift and the value of δ_{iso} indicate that the vanadium atom is located in an almost regular tetrahedral environment. According to data reported elsewhere,¹⁰⁷ the insignificant distortion of the tetrahe-

[†] Hereinafter, isothermal sections are shown in the phase diagrams.

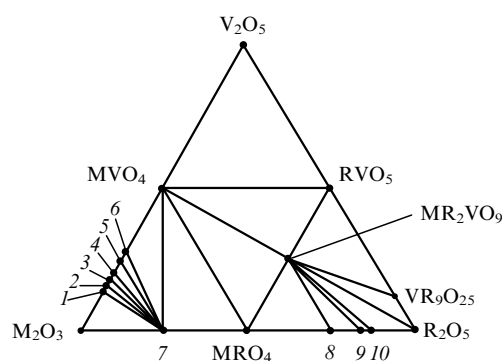


Figure 1. Phase relations in the $M_2O_3 - V_2O_5 - R_2O_5$ systems ($M = \text{REE}$, $R = \text{Ta, Nb}$).

(1) $M_{12}V_2O_{23}$ ($M = \text{Pr, Nd}$); (2) M_5VO_{10} ($M = \text{Y, Sm, Eu, Er}$); (3) $M_{1.62}V_{0.38}O_{3.38}$ ($M = \text{La, Nd, Eu, Gd, Tb}$); (4) $M_8V_2O_{17}$ ($M = \text{Y, La, Ce-Eu, Dy-Yb}$); (5) M_3VO_7 ($M = \text{La, Nd, Eu}$); (6) $La_{1.42}V_{0.58}O_{3.58}$; (7) M_3RO_7 ($R = \text{Ta, M} \neq \text{Ce}$; $R = \text{Nb, M} \neq \text{Sc, Ce}$); (8) MR_3O_9 ($R = \text{Ta, M} \neq \text{Sc}$; $R = \text{Nb, M} = \text{La-Sm}$); (9) MR_5O_{14} ($R = \text{Ta, M} = \text{La, Ce}$; $R = \text{Nb, M} = \text{La-Nd, Er}$); (10) MR_7O_{19} ($R = \text{Ta, M} \neq \text{Sc, Yb, Lu}$; $R = \text{Nb, M} = \text{La, Ce}$).

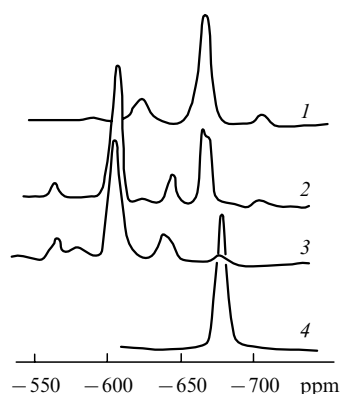


Figure 2. ^{51}V NMR spectra of YT_2VO_9 (1), YNb_2VO_9 (2), ScNb_2VO_9 (3), $\text{La}_4\text{VBO}_{10}$ (4).

dron can suggest that one of its oxygen atoms simultaneously belongs to an adjacent VO_4 tetrahedron. The NMR spectrum of the vanadatotantalate GdT_2VO_9 could not be recorded, probably due to quadrupole effects resulting in line broadening.

Thus, it is possible to distinguish a full isostoichiometric series in the LnTa_2VO_9 class of compounds (where Ln indicates lanthanides) existing at normal temperature and pressure. However, this is not a full isostructural series: for $\text{Ln} = \text{Gd}$, there is a morphotropic transition from one structural type ($\text{LnTa}_7\text{O}_{19}$) for $\text{Ln} = \text{Y}$, $\text{La} - \text{Eu}$ to another one for $\text{Ln} = \text{Gd} - \text{Lu}$.

III. Phase relations in the systems $\text{M}_2\text{O}_3 - \text{V}_2\text{O}_5 - \text{Nb}_2\text{O}_5$ ($\text{M} = \text{REE}$) and Y_2O_3 ($\text{La}_2\text{O}_3, \text{Sc}_2\text{O}_3$) - $\text{Nb}_2\text{O}_5 - \text{Ta}_2\text{O}_5$

Figure 1 shows phase relations in the $\text{M}_2\text{O}_3 - \text{V}_2\text{O}_5 - \text{Nb}_2\text{O}_5$ systems in the subsolidus region up to 1100°C (for $\text{M} = \text{Sc}$, up to 1000°C).^{83, 89, 94, 108–114} Compounds with the composition MNb_2VO_9 (henceforth referred to as vanadatoniobates) were found in ternary systems for every M.

Under isothermal annealing conditions at temperatures $> 900^\circ\text{C}$, the time required to establish equilibria in the $\text{M}_2\text{O}_3 - \text{Nb}_2\text{O}_5$ and $\text{V}_2\text{O}_5 - \text{Nb}_2\text{O}_5$ systems is the same as in the corresponding tantalum-containing systems. Ternary $\text{M}_2\text{O}_3 - \text{V}_2\text{O}_5 - \text{Nb}_2\text{O}_5$ systems come to equilibrium in 30–70 h.⁹ Vanadatoniobates decompose above 1150°C to give ortho- (Sc , Y) and metaniobates (La , Ln) and an unknown phase.⁸⁶ In the subsolidus region, all compounds of the ternary systems are stable.

The structure of vanadatoniobates has not been determined yet. According to SHG measurements, Sc , Y and La vanadatoniobates are centrosymmetrical crystals. It follows from comparison of the X-ray diffraction characteristics of MTa_2VO_9 and MNb_2VO_9 ($\text{M} = \text{Sc}$, Y , La) that ScTa_2VO_9 and ScNb_2VO_9 are isostructural; the structures of vanadatoniobates YNb_2VO_9 and LaNb_2VO_9 differ from each other and from those of vanadatotantalates YT_2VO_9 and LaTa_2VO_9 , respectively.

The structure of vanadatoniobates formed by cerium subgroup lanthanides differs from that of the corresponding vanadatotantalates. Within the series LnNb_2VO_9 ($\text{Ln} = \text{Ce} - \text{Eu}$), the structures of PrNb_2VO_9 and NdNb_2VO_9 are similar and differ from the structures of CeNb_2VO_9 , SmNb_2VO_9 and EuNb_2VO_9 , which have similar lattice symmetry. Probably, as in vanadatotantalates of cerium subgroup elements, the additional decrease in the energy of the f orbitals participating in the chemical bonds in vanadatoniobates of the elements of this subgroup affects the shape of the coordination polyhedra of the crystals.

The structure of vanadatoniobates of yttrium subgroup elements has some specific features. In the X-ray diffraction patterns of compounds in the series $\text{Gd} - \text{Lu}$, the interplanar distance (d) between the most intense reflexions decreases from 0.359 [relative

intensity (I/I_0) 69%] to 0.354 nm (relative intensity 68%) in the case of GdNb_2VO_9 and to 0.350 (relative intensity 100%) in the case of EuNb_2VO_9 . For TmNb_2VO_9 , YbNb_2VO_9 and LuNb_2VO_9 , only one reflexion with 100% intensity and $d = 0.351$ nm is observed. Thus, the vanadatoniobates LnNb_2VO_9 , where $\text{Ln} = \text{Gd}$, Tb , Dy , Ho , Er , are isostructural, and the structures differ from those of compounds with $\text{Ln} = \text{Tm}$, Yb , Lu . This behaviour is probably determined by the Ln^{3+} ionic radius and the degree of covalency of the $\text{Ln} - \text{O}$ bond. It should be noted that the structures of the cerium- and yttrium-subgroup compounds are different. The type of coordination polyhedron of the vanadatoniobate lattice was determined using NMR spectroscopy (see Fig. 2, curves 2,3).⁸³ In polycrystals of YNb_2VO_9 , the V^{5+} ions occupy two non-equivalent crystallographic positions. The isotropic shifts $\delta_{\text{iso}1}$ and $\delta_{\text{iso}2}$ are -665 ± 2 and -604 ± 2 , respectively, without the quadrupole correction. The small anisotropy and the magnitudes of the isotropic shifts suggest that the vanadium atom is located in an almost regular tetrahedral environment and can have one common atom with the adjacent VO_4 tetrahedron. It is of note that compounds YNb_2VO_9 and YT_2VO_9 are not isostructural but have almost similar tetrahedral environments with $\delta_{\text{iso}} = -665$.

Two lines are observed in the ^{51}V NMR spectrum of ScNb_2VO_9 . The use of the MAS technique made it possible to determine the isotropic shifts for these lines: -581 ± 5 (line I) and -603 ± 2 (line II). The presence of two lines in the spectrum suggests that the lattice contains two non-equivalent vanadium ions. The shape of line I implies an axial anisotropy of the chemical shift tensor equal to $\delta_{\perp} = -350$, whereas line II is almost symmetrical. The magnitude of anisotropy, its type and the magnitude of the isotropic shift make it possible to assume that line I belongs to the vanadium ions in a distorted octahedral environment, while line II belongs to the vanadium ions in a slightly distorted tetrahedral environment. The tetrahedral environments in ScNb_2VO_9 and in YNb_2VO_9 ($\delta_{\text{iso}} = -604$) are almost the same. In the vanadatoniobate ScNb_2VO_9 , the VO_4 tetrahedra are linked to each other through one common oxygen atom. The reason for distortion of the VO_6 octahedra is that each VO_6 octahedron has two common oxygen atoms with the adjacent octahedron.¹⁰⁷

Based on the X-ray diffraction characteristics obtained for LnNb_2VO_9 ($\text{Ln} = \text{REE}$), it can be stated that this isostoichiometric series of compounds is not a full isostructural series. Five different structure types exist in the series of LnNb_2VO_4 vanadatoniobates: the first one for $\text{Ln} = \text{La}$, the second one for $\text{Ln} = \text{Pr}$ and Nd , the third one for $\text{Ln} = \text{Ce}$, Sm and Eu , the fourth one for $\text{Ln} = \text{Gd}$, Tb , Dy , Ho , Er and the fifth one for $\text{Ln} = \text{Tm}$, Yb and Lu . Thus, a morphotropy phenomenon is observed.

The $\text{Y}_2\text{O}_3 - \text{Nb}_2\text{O}_5 - \text{Ta}_2\text{O}_5$ system.¹¹⁵ Figure 3 presents phase relations in the $\text{Y}_2\text{O}_3 - \text{Nb}_2\text{O}_5 - \text{Ta}_2\text{O}_5$ system in a subsoli-

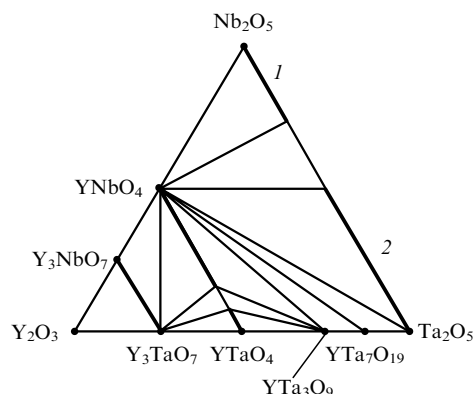


Figure 3. Phase relations in the $\text{Y}_2\text{O}_3 - \text{Nb}_2\text{O}_5 - \text{Ta}_2\text{O}_5$ system. (1) $\alpha\text{-Nb}_{2(1-x)}\text{Ta}_{2x}\text{O}_5$; (2) $\beta\text{-Ta}_{2(1-x)}\text{Nb}_{2x}\text{O}_5$.

dus region up to 1350 °C. Solid solutions in this system were studied by optical-immersion analysis. A continuous series of solid solutions with the compositions $Y_3Nb_xTa_{1-x}O_7$ with a probable structure of the pyrochlore type was found in the quasibinary section Y_3TaO_7 – Y_3NbO_7 , and solid solutions of two types were found in the quasibinary section $YTaO_4$ – $YNbO_4$. The first type has the composition $YNb_xTa_{1-x}O_4$ and is based on the fergusonite M' -modification in the concentration range $0 \leq x \leq 0.15$, while the second type has the same composition and is based on the fergusonite M -modification in the concentration range $0.3 \leq x \leq 1$. A mixture of solid solutions of the first and second types is formed in the intermediate region, viz., $0.15 < x < 0.3$. Above 1400 °C, a continuous series of solid solutions with M -fergusonite structure exists in this section.

The La_2O_3 – Nb_2O_5 – Ta_2O_5 system.¹¹⁶ In order to determine the location of the quasibinary sections and to perform the triangulation of the La_2O_3 – Nb_2O_5 – Ta_2O_5 system, physicochemical analysis was used to study the phase composition of 30 points located in various hypothetical sections and regions of the system. Figure 4 presents phase relations in the La_2O_3 – Nb_2O_5 – Ta_2O_5 system in a subsolidus region up to 1250 °C. Various solid substitution solutions were found in the region containing more than 50 mol. % La_2O_3 . The hatched regions 1 and 2 contain solid solutions based on $LaNbO_4$ and La_3NbO_7 , respectively. In addition, a limited series of solid solutions of the general formula $LaTa_{1-x}Nb_xO_4$ ($0 \leq x \leq 0.15$) based on $LaTaO_4$ was found in the $LaNbO_4$ – $LaTaO_4$ section. A continuous series of solid solutions of the general formula $La_3Nb_{1-y}Ta_yO_7$ ($0 \leq y \leq 1$) exists in the La_3NbO_7 – La_3TaO_7 section.

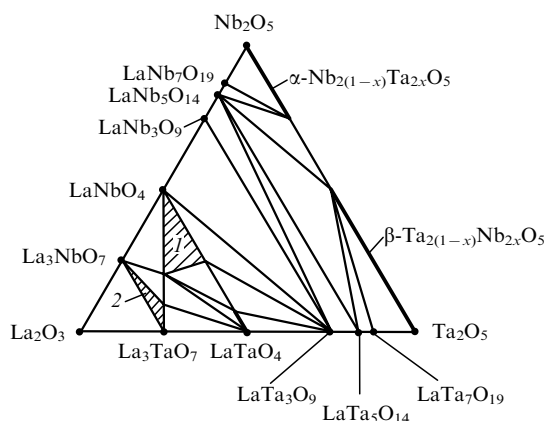


Figure 4. Phase relations in the La_2O_3 – Nb_2O_5 – Ta_2O_5 system. The hatched zones indicate the areas of existence of solid solutions based on $LaNbO_4$ (1) and La_3NbO_7 (2).

The Sc_2O_3 – Nb_2O_5 – Ta_2O_5 system.[§] The phase composition of the system was studied up to 1400 °C; no ternary compounds were found (Fig. 5). A continuous series of solid substitution solutions of the general formula $ScTa_{1-x}Nb_xO_4$ with the wolframite structure exists in the quasibinary section $ScNbO_4$ – $ScTaO_4$.

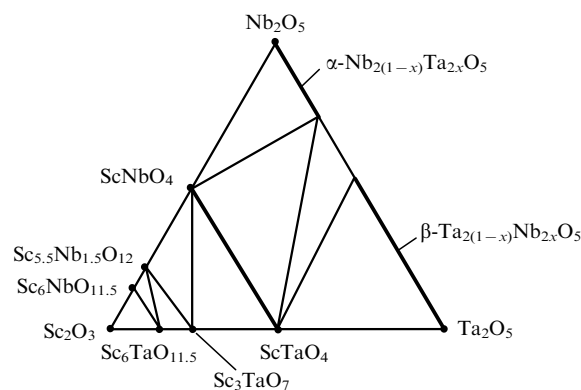


Figure 5. Phase relations in the Sc_2O_3 – Nb_2O_5 – Ta_2O_5 system.

IV. Phase relations in systems containing B, Al and Ga

The M_2O_3 – B_2O_3 – Ta_2O_5 systems.^{83, 117–119} Figure 6a,b presents phase relations in the Sc_2O_3 – B_2O_3 – Ta_2O_5 and Y_2O_3 – B_2O_3 – Ta_2O_5 systems in a subsolidus region up to 1100 °C. No ternary compounds were found in these systems.

Figure 7 demonstrates phase relations in the La_2O_3 – B_2O_3 – Ta_2O_5 system in a subsolidus region up to 1000 °C. A ternary compound with the composition $LaTaB_2O_7$, which exists in

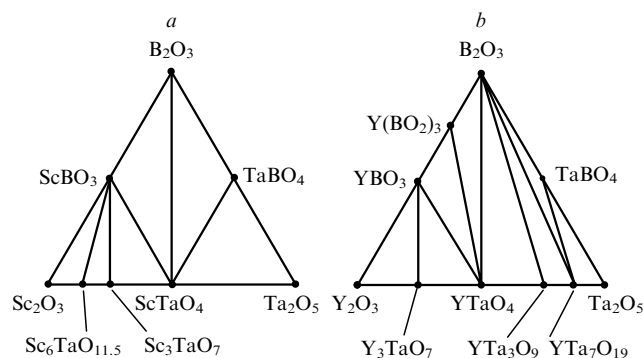


Figure 6. Phase relations in the Sc_2O_3 – B_2O_3 – Ta_2O_5 (a) and Y_2O_3 – B_2O_3 – Ta_2O_5 (b) systems.

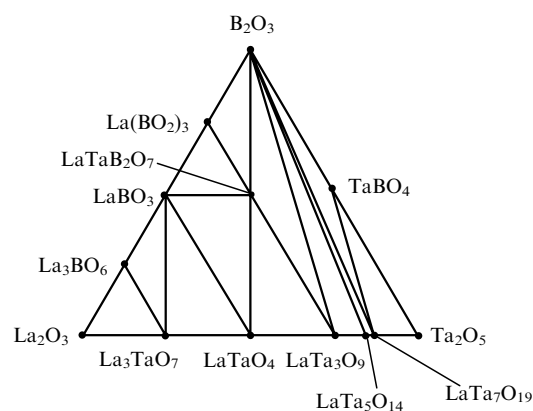


Figure 7. Phase relations in the La_2O_3 – B_2O_3 – Ta_2O_5 system.

§The system was studied by E V Arkhipova (Institute of Solid State Chemistry of the Urals Branch of the Russian Academy of Sciences).

equilibrium with LaBO_3 , $\text{La}(\text{BO}_2)_3$, B_2O_3 , LaTa_3O_9 and LaTaO_4 , was found in the quasibinary section $\text{La}(\text{BO}_2)_3$ – LaTa_3O_9 . Lanthanum boratotantalate decomposes at $\sim 1200^\circ\text{C}$ in accordance with the peritectic reaction



In the M_2O_3 – B_2O_3 systems, thermodynamic equilibrium at temperatures above 1000°C is established in several tens of hours.⁶⁶ The time required to reach equilibrium in ternary systems is even longer, viz., ~ 200 h.⁹ All phases of the systems described above are stable in a subsolidus region.

According to SHG laser irradiation measurements, lanthanum boratotantalate has centrosymmetrical crystals. X-Ray diffraction studies suggest that it has orthorhombic symmetry. The unit cell parameters a , b and c for LaTaB_2O_7 are 1.28692, 1.17562 and 1.13692 nm, respectively; the unit cell volume is 1.72004 nm^3 ; the number of formula units in the lattice (z) is 14; the picnometric density is $6.16 \times 10^3\text{ kg m}^{-3}$.

The coordination of boron in these crystals was studied by NMR spectroscopy.¹²⁰ Figure 8 shows the ^{11}B NMR spectrum of the boratotantalate LaTaB_2O_7 (relative to aqueous H_3BO_3 , magic-angle spinning). The spectrum is a superposition of two doublet components ($\delta = -7.96$ and -21.59) and a narrow central peak ($\delta = -16.53$). The assignment was made using the known literature data (see, e.g., Ref. 121). It was found that the doublet belongs to the boron nuclei located in a trigonal oxygen environment (the quadrupole coupling constant is 2.5 MHz), while the narrow line belongs to the boron nuclei in a tetrahedral environment. It should be noted that the central component in the spectra is shifted by 7 ppm, and the doublet is shifted by 14 ppm with respect to diamagnetic compounds. This is probably caused by paramagnetic admixtures in the samples.

The ternary M_2O_3 – B_2O_3 – Ta_2O_5 systems with the following lanthanides were studied: cerium, praseodymium, neodymium, samarium and europium.^{122,123} No ternary compounds were found in these systems. Figure 9 *a, b* presents phase relations in

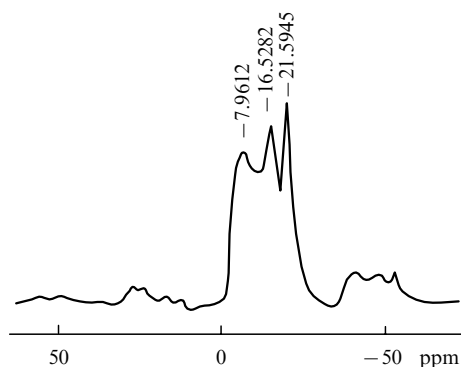


Figure 8. ^{11}B NMR spectrum of boratotantalate LaTaB_2O_7 .

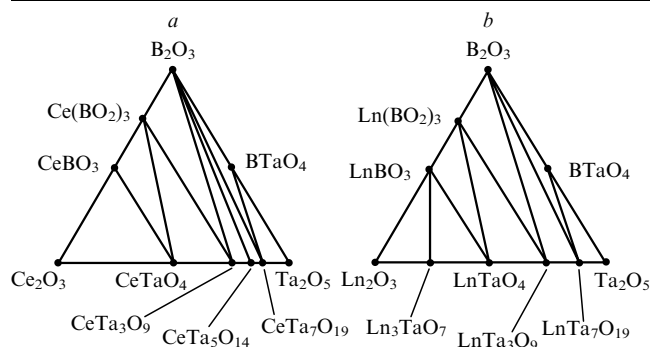


Figure 9. Phase relations in the Ce_2O_3 – B_2O_3 – Ta_2O_5 (*a*) and Ln_2O_3 – B_2O_3 – Ta_2O_5 ($\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}$) (*b*) systems.

these systems in a subsolidus region up to 1000°C . It is seen that borates are in equilibrium with lanthanide tantalates.

The M_2O_3 – B_2O_3 – Nb_2O_5 systems.^{83,118,119} These systems, where $\text{M} = \text{REE}$, are similar to the corresponding tantalum-containing ternary systems in many respects. The equilibrium in these systems is also established in ~ 200 h.⁹ No ternary compounds were found in the Sc_2O_3 – B_2O_3 – Nb_2O_5 and Y_2O_3 – B_2O_3 – Nb_2O_5 systems, the phase relations in which in a subsolidus region up to 1000°C are presented in Fig. 10 *a, b*.

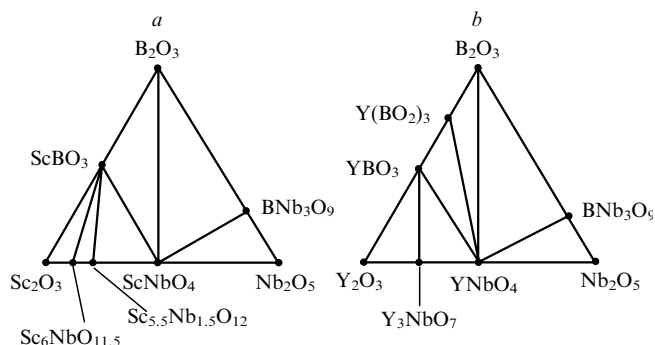


Figure 10. Phase relations in the Sc_2O_3 – B_2O_3 – Nb_2O_5 (*a*) and Y_2O_3 – B_2O_3 – Nb_2O_5 (*b*) systems.

More complex phase relations are observed in the La_2O_3 – B_2O_3 – Nb_2O_5 system.^{117,119} The ternary compound LaNbB_2O_7 is formed in this system; this compound exists in equilibrium with LaNbO_4 , LaNb_3O_9 , LaBO_3 , $\text{La}(\text{BO}_2)_3$ and B_2O_3 . The boratonio-bate LaNbB_2O_7 is isostructural to the boratotantalate LaTaB_2O_7 . It decomposes peritectically above 1200°C to give LaNbO_4 and B_2O_3 . Figure 11 shows phase relations in this system in a subsolidus region up to 1000°C . The unit cell parameters a , b and c of LaNbB_2O_7 are 1.2771(5), 1.1722(5) and 1.1223(5) nm; the unit cell volume is 1.679231 nm^3 .

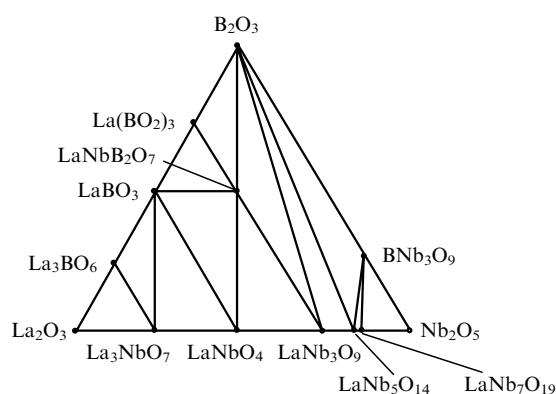


Figure 11. Phase relations in the La_2O_3 – B_2O_3 – Nb_2O_5 system.

The M_2O_3 – B_2O_3 – V_2O_5 systems. The equilibrium in these systems is established in more than 800 h,⁹ which is much longer than in the M_2O_3 – B_2O_3 – R_2O_5 systems ($\text{R} = \text{Ta}, \text{Nb}$).

Figure 12 demonstrates phase relations in the Y_2O_3 – B_2O_3 – V_2O_5 system in a subsolidus region up to 1000°C . No ternary compounds were found in this system.¹²⁴

Figure 13 presents phase relations in the La_2O_3 – B_2O_3 – V_2O_5 system in a subsolidus region up to 900°C .¹²⁵ It was found that lanthanum orthovanadate is in equilibrium with all compounds of the binary systems La_2O_3 – B_2O_3 and B_2O_3 – V_2O_5 except La_3BO_6 . A ternary compound with the composition $\text{La}_4\text{VBO}_{10}$ is formed in this system in the region with high La_2O_3 content; this compound

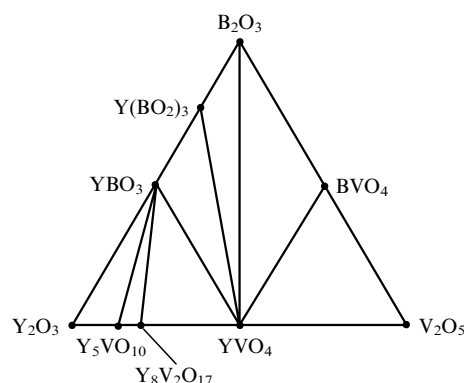


Figure 12. Phase relations in the Y_2O_3 – B_2O_3 – V_2O_5 system.

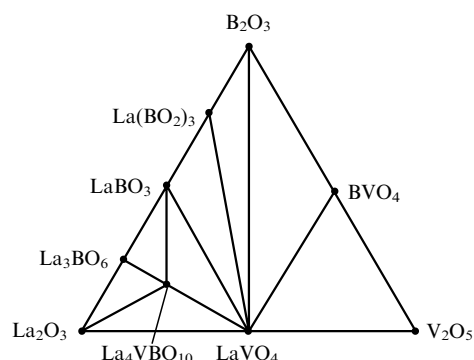


Figure 13. Phase relations in the La_2O_3 – B_2O_3 – V_2O_5 system.

is in equilibrium with La_2O_3 , La_3BO_6 , LaBO_3 and LaVO_4 . The melting point of $\text{La}_4\text{VBO}_{10}$ is unknown. According to SHG measurements, this compound has centrosymmetrical crystals.

Figure 2 (curve 4) shows the ^{51}V NMR spectrum of $\text{La}_4\text{VBO}_{10}$ polycrystals. The spectrum is a single line with $\delta_{\text{iso}} = -674$. The magnitude of the quadrupole correction indicates that vanadium is located in a nearly regular tetrahedral environment.¹²⁶ As in vanadatoniobates, the VO_4 tetrahedra can have one common oxygen atom with the adjacent tetrahedra. The signal of the boron nuclei is very weak, probably due to quadrupole effects.

Hence, LaTaB_2O_7 , LaNbB_2O_7 and $\text{La}_4\text{VBO}_{10}$ are merely the first members of the corresponding isostoichiometric series under ordinary conditions. An attempt to obtain compounds of scandium, yttrium and lanthanides with compositions indicated above failed.⁸³

Gokhman *et al.*¹²⁷ synthesised ternary oxides with the composition $\text{Ln}_7\text{V}_2\text{BO}_{17}$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$). The samples were obtained in air by multi-step sintering of the starting oxides Ln_2O_3 , V_2O_5 and H_3BO_3 . The temperature of the final sintering step was 1240°C ; the overall sintering time was 30 h. The melting points of the compounds are unknown. Ternary oxides for $\text{Ln} = \text{Sm}, \text{Eu}, \text{Gd}$ and Tb could not be obtained. Table 2 lists the unit cell parameters for the crystals of $\text{Ln}_7\text{V}_2\text{BO}_{17}$, which possess monoclinic symmetry.

Table 2. Unit cell parameters of $\text{Ln}_7\text{V}_2\text{BO}_{17}$ crystals.

Ln	<i>a</i> /nm	<i>b</i> /nm	<i>c</i> /nm	β /deg	<i>V</i> /nm ³
La	0.695(1)	1.786(1)	1.227(1)	99.6(1)	1.501(2)
Pr	0.687(1)	1.747(7)	1.205(3)	99.7(3)	1.425(7)
Nd	0.680(1)	1.723(2)	1.205(1)	99.4(1)	1.392(2)

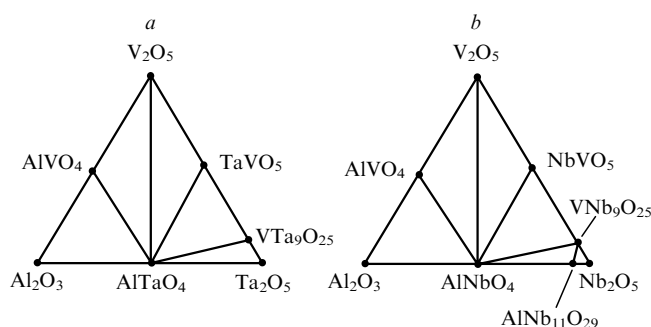


Figure 14. Phase relations in the Al_2O_3 – V_2O_5 – Ta_2O_5 (a) and Al_2O_3 – V_2O_5 – Nb_2O_5 (b) systems.

The Al_2O_3 – V_2O_5 – R_2O_5 systems. Figure 14a shows phase relations in the Al_2O_3 – V_2O_5 – Ta_2O_5 system in a subsolidus region up to 1350°C , and Fig. 14b shows phase relations in the Al_2O_3 – V_2O_5 – Nb_2O_5 system in a subsolidus region up to 1100°C . The times required to establish equilibria in these systems are the same as those for M_2O_3 – V_2O_5 – R_2O_5 ($\text{M} = \text{REE}$, $\text{R} = \text{Ta}, \text{Nb}$). No ternary compounds were found in these systems.^{9, 128–130}

It was found that the AlTaO_4 phase has two crystal modifications in the section AlTaO_4 – V_2O_5 (see Fig. 14a). In the vicinity of the section point where the concentrations of the components, *i.e.*, Al_2O_3 , V_2O_5 and Ta_2O_5 , are 38 mol.%, 24 mol.% and 38 mol.%, respectively, the AlTaO_4 crystals are isostructural to alumotantite (its formula is $\text{Al}_{0.98}\text{Ta}_{0.99}\text{Nb}_{0.02}\text{O}_4$) with orthorhombic symmetry.¹³¹ In the other points of this section studied, the AlTaO_4 crystals have a structure different from that of alumotantite.¹³² It should also be noted that for all points of this section containing less than 50 mol. % V_2O_5 (except for the point specified above), the diffractograms of freshly prepared AlTaO_4 samples recorded at room temperature contain additional lines. These lines disappear after storage of the samples in air for a month. These reflexions probably originate from structural ordering of AlTaO_4 crystals with involvement of lattice defects.

The AlNbO_4 structure is described in the database of X-ray spectra.¹³³

The M_2O_3 – Ga_2O_3 – Nb_2O_5 (Ta_2O_5) systems ($\text{M} = \text{La}, \text{Pr}$).⁴² The isothermal sections in these systems have not been studied. It was found that the La_2O_3 – Ga_2O_3 – Nb_2O_5 system contains a ternary compound with the composition $\text{La}_3\text{Ga}_{5.5}\text{Nb}_{0.5}\text{O}_{14}$ having the structure of $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ ($a = 0.8218$ nm, $c = 0.5122$ nm; the densities obtained from X-ray estimation and from experimental measurement are 5.934×10^3 and 5.903×10^3 kg m^{−3}, respectively). The compound has a narrow homogeneity range and is stable up to 1450°C .

The compound $\text{La}_3\text{Ga}_{5.5}\text{Ta}_{0.5}\text{O}_{14}$ ($a = 0.8151$ nm, $c = 0.5105$ nm) is formed in the La_2O_3 – Ga_2O_3 – Ta_2O_5 system, and the compounds $\text{Pr}_3\text{Ga}_{5.5}\text{Nb}(\text{Ta})_{0.5}\text{O}_{14}$ exist in the Pr_2O_3 – Ga_2O_3 – Nb_2O_5 (Ta_2O_5) systems. Starting with $\text{M} = \text{Nd}$, no similar compounds isostructural to $\text{Ca}_3\text{Ga}_2\text{Ge}_4\text{O}_{14}$ are formed.

V. Phase formation regularities in ternary systems

It follows from the experimental phase relation diagrams that vanadatoniobates MNb_2VO_9 exist in equilibrium preferentially with compounds which have the structural type of fergusonite, perovskite, zircon, wolframite (ScNbO_4) and with compounds α - $\text{LaNb}_5\text{O}_{14}$ and $\text{MNb}_7\text{O}_{19}$ ($\text{M} = \text{La}, \text{Ce}$). Vanadatotantalates MTa_2VO_9 coexist with such compounds as fergusonite, perovskite, wolframite (ScTaO_4), LaTaO_4 , $\text{MTa}_5\text{O}_{14}$ ($\text{M} = \text{La}, \text{Ce}$) and with compounds of hexagonal symmetry such as $\text{MTa}_7\text{O}_{19}$. All vanadatotantalates and -niobates exist in equilibrium with tetragonal phases such as VR_9O_{25} and RVO_5 ($\text{R} = \text{Ta}, \text{Nb}$). Lanthanum boratotantalate and -niobate LaRB_2O_7 ($\text{R} = \text{Ta}, \text{Nb}$) coexist

Table 3. Ionic sizes (Ref. 134) of Group III and VB elements and ratios of ionic radii.

Ion (1) ^a	Radius (r_1) /nm	Ion (2) ^a	Radius (r_2) /nm	r_1/r_2
B^{3+} (3)	0.01	V^{5+} (4)	0.0355	~ 0.3
		Nb^{5+} (4)	0.048	~ 0.2
		Nb^{5+} (6)	0.064	~ 0.16
		Ta^{5+} (6)	0.064	~ 0.16
V^{5+} (4)	0.0355	Nb^{5+} (4)	0.048	~ 0.74
		Nb^{5+} (6)	0.064	~ 0.55
		Ta^{5+} (6)	0.064	~ 0.55
Ga^{3+}	0.047–0.062 ^b			

^a The numbers in parentheses indicate the coordination numbers. ^b Values for different coordination numbers are given.

with such compounds as perovskite, aragonite, fergusonite, $LaRO_4$ and monoclinic $La(BO_2)_3$, whereas lanthanum boratovanadate La_4VBO_{10} coexists with such compounds as monazite, aragonite and monoclinic La_3BO_6 . All ternary compounds described above exist in equilibrium with simple oxides R_2O_5 ($R = Ta, Nb, V$), B_2O_3 , La_2O_3 .

Solid solutions in the $Y_2O_3-Nb_2O_5-Ta_2O_5$ system coexist with such compounds as fergusonite, pyrochlore, perovskite, Y_2O_3 , R_2O_5 ($R = Ta, Nb$); those in the $La_2O_3-Nb_2O_5-Ta_2O_5$ system coexist with such compounds as weberite, perovskite, $LaTaO_4$ and La_2O_3 , and those in the $Sc_2O_3-Nb_2O_5-Ta_2O_5$ system coexist with such oxides as Sc_3TaO_7 and R_2O_5 ($R = Nb, Ta$).

Thus, it can be stated that ternary phases formed in systems of Group III and VB oxides (except for $La_2O_3-B_2O_3-V_2O_5$) exist in equilibrium with compounds that have the fergusonite and perovskite structural types and with compounds characteristic of each individual system.

It is well known that no theory formulating the phase formation criteria in complex systems exists at present. The phase formation in quasi-binary vanadate systems was analysed by estimation of cation radii and with the use of the spatial-energetical P parameter.⁴⁴

Let us consider the regularities in the formation of mixed crystals for Group III and VB elements depending on the ion sizes and on the ionic radii ratios in ternary compounds (Table 3).

If the ratio of the ionic radius of boron to that of tantalum or niobium is ~ 0.2 , no ternary compounds of lanthanides, scandium and yttrium are formed in the $M_2O_3-B_2O_3-Ta_2O_5$ (Nb_2O_5) systems ($M = Sc, Y, Ce-Lu$). The existence of the starting

Table 4. Ratios of ionic radii in ternary compounds.

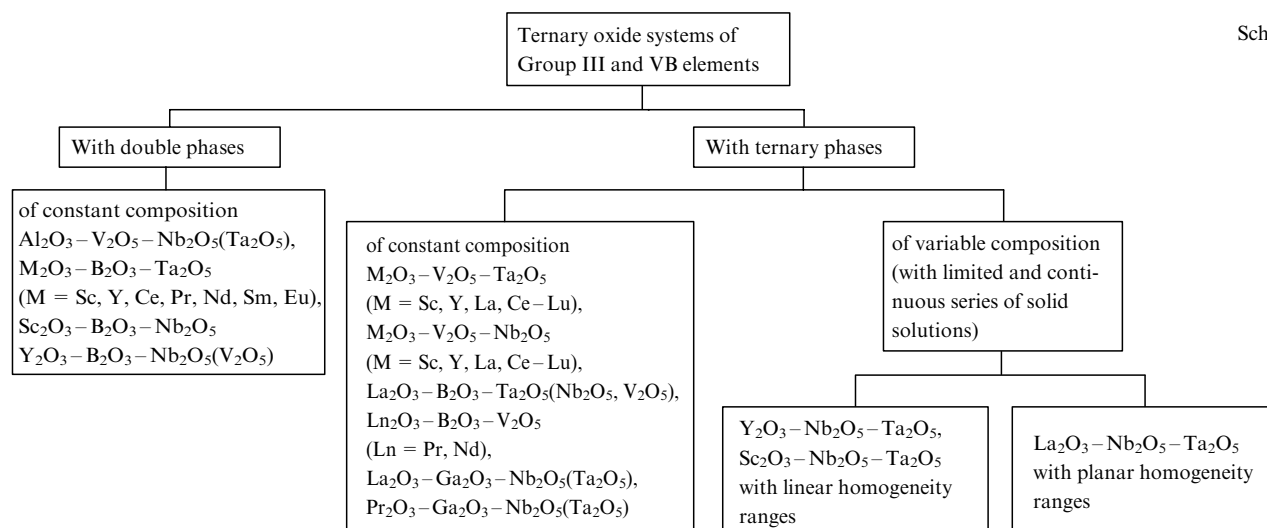
Compounds	M	Ion (1)	Ion (2)	r_1/r_2
MR_2VO_9 ($R = Nb, Ta$)	Sc, Y, La–Lu	V^{5+}	R^{5+}	0.55–0.74
MRB_2O_7 ($R = Nb, Ta$)	La	B^{3+}	R^{5+}	0.2
M_4VBO_{10}	La	B^{3+}	V^{5+}	0.3
$M_7V_2BO_{17}$	La, Pr, Nd	B^{3+}	V^{5+}	0.3
$M_3Ga_{5.5}R_{0.5}O_{14}$ ($R = Nb, Ta$)	La, Pr	Ga^{3+}	R^{5+}	0.97

members of the series with $M = La$, viz., $LaTaB_2O_7$ and $LaNbB_2O_7$, can be explained by the fact that the radius of the La^{3+} ion is larger than those of scandium and lanthanides. In the $Al_2O_3-V_2O_5-Ta_2O_5$ (Nb_2O_5) systems, ternary compounds with hypothetical composition $Al_xTa(Nb)_yV_zO_k$ are not formed, either. Probably, the cation radii should also be taken into account in addition to the ionic radii ratios in the anionic parts of the compounds. The ion radius of Al^{3+} is 0.0390 to 0.0535 nm depending on the coordination number; it is smaller than the ion radii of scandium, yttrium, lanthanum and lanthanides. This is probably the reason why ternary compounds are not formed in the $Al_2O_3-V_2O_5-Ta_2O_5$ (Nb_2O_5) systems [unlike in the $M_2O_3-V_2O_5-Ta_2O_5$ (Nb_2O_5) systems ($M = Sc, Y, La-Lu$) where the MR_2VO_9 compounds exist]. In the $M_2O_3-B_2O_3-V_2O_5$ systems ($M = La, Pr, Nd$) at temperatures $> 900^\circ C$, the $M_7V_2BO_{17}$ compounds exist (see Ref. 127), whereas only one compound, namely, M_4VBO_{10} with $M = La$, was found at temperatures $< 900^\circ C$. Hence, one can probably expect the formation of compounds with molecular composition M_4VBO_{10} for $M = Pr$ and Nd .

Thus, the dimension-related criterion for the formation of ternary compounds in oxide systems includes two conditions: (1) the cation radius should be larger than 0.0535 nm; (2) the radii ratios for the ions forming the anionic parts should be greater than 0.2 but smaller than 1. It follows from the data in Table 4 that if the ionic radii ratio is $r_1/r_2 \approx 0.2$, ternary compounds exist only in the case of $M = La$, whereas if this ratio is 0.55–0.74, these exist in the case of $M = Sc, Y, La-Lu$. However, if the radius of the M ion is smaller than that of the Sc ion, ternary compounds are not formed for $r_1/r_2 = 0.55-0.74$ [where $ion(1) = V^{5+}$; $ion(2) = Ta^{5+}, Nb^{5+}$]. In the $M_2O_3-Nb_2O_5-Ta_2O_5$ systems, no ternary compounds with hypothetical composition $M_xNb_yTa_zO_r$ are formed either if $r_1/r_2 = 1$ and $M = Sc, Y, La$.

Thus, the following classification of ternary oxide systems of Group III and VB elements can be made: (1) systems with an equilibrium between the original components and binary compounds; (2) systems where ternary phases are formed. In turn,

Scheme 1



ternary phases can have a constant composition (chemical compounds) or a variable composition (solid solutions). The arbitrary character of this classification is due to the fact that constant composition phases always contain very narrow homogeneity regions which can be neglected. Scheme 1 shows the classification of ternary oxide systems; this classification can apparently be used to predict the existence of phase equilibria, *e.g.*, in the $\text{Ln}_2\text{O}_3\text{--Nb}_2\text{O}_5\text{--Ta}_2\text{O}_5$ and $\text{Ln}'_2\text{O}_3\text{--Nb}_2\text{O}_5\text{--Ta}_2\text{O}_5$ systems, where Ln and Ln' are lanthanides belonging to the yttrium and cerium subgroups, respectively.

VI. Vibrational spectra of ternary oxides

Using NMR spectroscopy in MR_2VO_9 ($R = \text{Ta}, \text{Nb}$) and $\text{La}_4\text{VBO}_{10}$ crystals, the VO_4 and VO_6 anionic groups were revealed; they are generally linked through one or two oxygen atoms with the adjacent VO_4 or VO_6 groups, respectively. The LaTaB_2O_7 crystals were shown to contain BO_3 triangles. Thus, one of the goals in the analysis of the vibrational spectra of ternary oxides is to determine whether the anionic part of a compound is a united complex anion or it consists of anionic groups.

1. MTa_2VO_9 crystals

The IR spectra of the MTa_2VO_9 crystals, where M indicates cerium subgroup elements, contain narrow intense bands in the range of $430\text{--}437\text{ cm}^{-1}$, whereas the remaining bands in the spectrum are broad and have medium intensity. The band positions in the range of $600\text{--}900\text{ cm}^{-1}$ depend on the nature of the M^{3+} ion: the vibration frequencies are shifted to the long-wave region with a decrease in the ionic radii in the series Ce–Eu (Fig. 15). It is well known that a decrease in the ionic radius increases the covalence of bond between a lanthanide ion and the environment and enhances the effect of the crystal field,¹¹ hence these bands can originate from the stretching vibrations of the Ta–O bonds involving the M–O bonds. The shape of the IR spectra of MTa_2VO_9 crystals, where M indicates yttrium subgroup elements, depends on the nature of the metal and changes non-monotonically (Fig. 16).⁸⁸

The most significant differences between the spectra of MTa_2VO_9 , where M indicates yttrium and cerium subgroup elements, are observed in the region of $200\text{--}500\text{ cm}^{-1}$, which probably corresponds to the deformation vibrations of the lattice polyhedra. The IR spectra of LaTa_2VO_9 (Fig. 17, spectrum 1) and ScTa_2VO_9 (Fig. 17, spectrum 3) are similar to the spectra of MTa_2VO_9 , where M indicates yttrium and cerium subgroup elements, respectively. Replacement of 50% of yttrium in YT_2VO_9 by europium stabilises the α -phase, and the IR spectrum of the solid solution $\text{Y}_{0.5}\text{Eu}_{0.5}\text{Ta}_2\text{VO}_9$ (Fig. 17, spectrum 2)

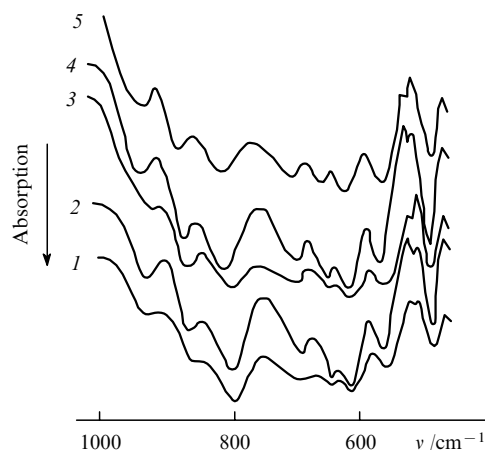


Figure 15. IR spectra of MTa_2VO_9 , where M = Ce (1), Pr (2), Nd (3), Sm (4), Eu (5).

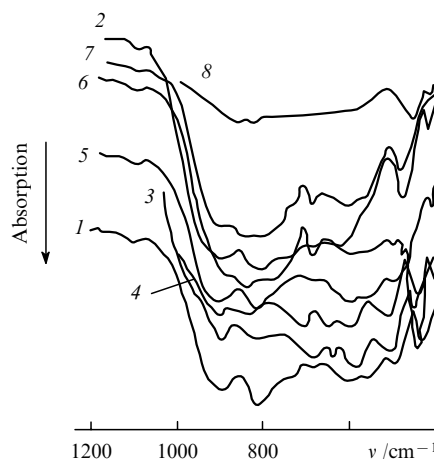


Figure 16. IR spectra of MTa_2VO_9 , where M = Gd (1), Tb (2), Dy (3), Ho (4), Er (5), Tm (6), Yb (7), Lu (8).

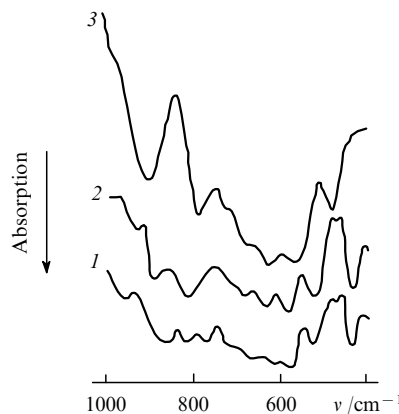


Figure 17. IR spectra of LaTa_2VO_9 (1), $\text{Y}_{0.5}\text{Eu}_{0.5}\text{Ta}_2\text{VO}_9$ (2) and ScTa_2VO_9 (3).

resembles that of LaTa_2VO_9 . Tables 5–8 list the frequencies of vibrational spectrum maxima for compounds of the general formula MTa_2VO_9 ($M = \text{Sc}, \text{Y}, \text{La--Lu}$). The bands in the regions of $865\text{--}900$, $790\text{--}835$, $455\text{--}485$ and $370\text{--}385\text{ cm}^{-1}$ can probably be assigned to the ν_1 , ν_3 , ν_4 and ν_2 vibrations of the VO_4 tetrahedra, respectively, while the bands in the regions of $910\text{--}930$, $580\text{--}710$ and $430\text{--}455\text{ cm}^{-1}$ can be assigned to the ν_1 , ν_3 and ν_5 vibrations of the TaO_6 octahedra, respectively. Only the most intense lines in the Raman spectra of LaTa_2VO_9 and TbTa_2VO_9 were recorded.[¶] The Raman spectra of the vanadotantalates CeTa_2VO_9 and ScTa_2VO_9 could not be recorded, probably due to strong absorption of radiation.

The Raman spectra of MTa_2VO_9 , where $M = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Tm}, \text{Yb}, \text{Lu}$, in the region of $780\text{--}1000\text{ cm}^{-1}$ are similar (Fig. 18–20): each of them contains an intense line at $855\text{--}900\text{ cm}^{-1}$ and two lines around $780\text{--}835\text{ cm}^{-1}$. The differences between the spectra of the compounds containing cerium and yttrium subgroup elements are mostly observed in the range below 780 cm^{-1} . The Raman spectra of the vanadotantalates HoTa_2VO_9 and ErTa_2VO_9 differ from those described above (see Fig. 19, spectra 2 and 3). The spectrum of HoTa_2VO_9 was recorded using argon laser excitation (excitation with a helium–neon laser results in a weak vibrational spectrum at the background level). It contains a group of narrow high-intensity lines at

[¶]All Raman spectra were recorded with excitation by a helium–neon laser ($\lambda = 632.8\text{ nm}$) unless stated otherwise.

Table 5. Frequencies (cm^{-1}) of maxima in vibrational spectra of MTa_2VO_9 ($M = \text{La, Ce, Pr, Nd}$).

La		Ce (IR)	Pr		Nd		Assignment
IR	Raman		IR	Raman	IR	Raman	
—	—	—	—	—	—	1150	stretching vibrations of VO_4 , TaO_6 , VO_6
—	—	—	—	990	—	990	
965	—	957	960	—	940	—	
885	—	—	885	890	884	—	
860	—	873	—	—	—	—	
—	870	—	—	855	—	870	
—	845	—	—	—	—	—	
826	—	800	802	820	802	—	
808	—	—	—	790	—	—	
—	—	—	—	780	—	795	
783	—	—	—	—	—	785	
—	—	—	—	750	—	760	
675	—	677	679	—	683	—	
—	—	—	—	650	—	—	
620	—	—	623	—	626	—	
—	—	618	—	—	—	610	deformation vibrations of VO_4 , TaO_6 , VO_6
585	—	585	592	570	590	—	
525	—	520	530	530	527	535	
475	—	467	469	—	472	—	
—	—	—	—	460	—	470	
440	435	431	437	—	437	450	
—	380	—	—	420	—	—	
—	—	—	—	370	—	370	
—	—	—	—	—	360	—	
—	—	—	—	350	—	350	
—	—	—	—	305	—	305	$\nu(\text{M}-\text{O})$
—	—	—	—	290	270	—	
—	—	—	—	250	—	245	
—	—	—	—	225, 215, 180, 155, 110, 75, 70	—	225	translation and rotation of VO_4 , VO_6

910, 930, 940(sh.), 985, 1000 and 1045 cm^{-1} . These lines may be due to resonance phenomena caused by diffusion of laser light near the $^5\text{F}_4$ state of the Ho^{3+} ion. The spectrum of ErTa_2VO_9

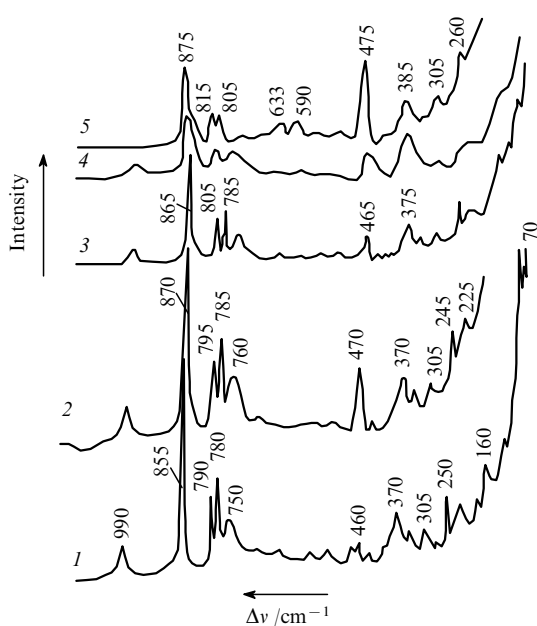
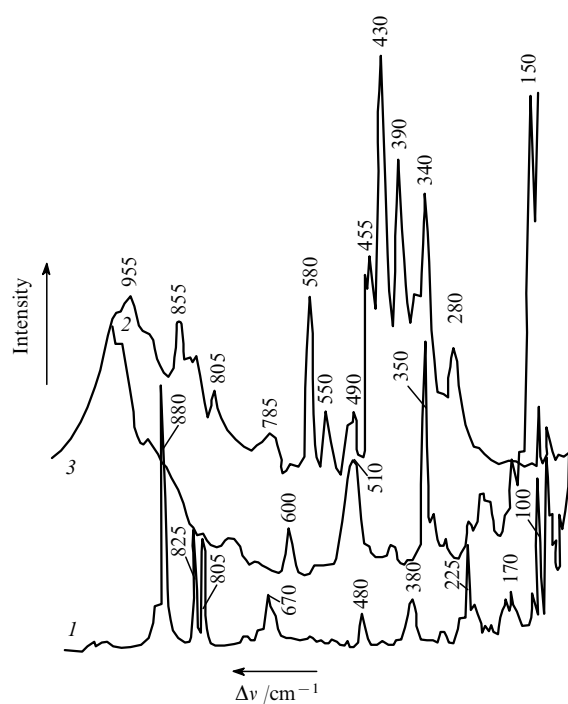
**Figure 18.** Raman spectra of MTa_2VO_9 , where $M = \text{Pr}$ (1), Nd (2), Sm (3), Eu (4), Gd (5).**Figure 19.** Raman spectra of MTa_2VO_9 , where $M = \text{Dy}$ (1), Ho (2), Er (3).

Table 6. Frequencies (cm^{-1}) of maxima in vibrational spectra of MTa_2VO_9 ($M = \text{Sm, Eu, Gd, Tb}$).

Sm		Eu		Gd		Tb		Assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	
—	—	—	—	—	—	—	1080	stretching vibrations of VO_4 , TaO_6 , VO_6
—	990	—	990	—	—	—	—	
960	—	940	—	—	—	—	—	
887	—	884	—	895	—	895	—	
—	865	—	870	—	875	—	900	
—	845	—	—	—	840	—	—	
810	805	802	—	810	—	810	—	
—	790	—	825	—	815	—	—	
—	—	—	780	—	805	—	—	
—	—	—	—	—	770	—	—	
—	750	—	—	735(sh)	—	735	—	
682	675	683	690	680	670	681	—	
—	—	—	—	—	635	—	—	
627	625	626	—	—	—	—	—	
—	—	—	610	—	—	—	—	
590	580	590	560	595	590	590	—	deformation vibrations of VO_4 , TaO_6 , VO_6
530	510	527	—	550	535	550	—	
469	470	—	—	490	475	—	—	
—	445	—	485	—	—	490	—	
433	—	437	—	—	—	—	—	
398	415	398	—	400(sh)	—	—	—	
—	370	—	385	—	385	—	—	
360	—	362	—	364	—	—	—	$\nu(\text{M}-\text{O})$
336	345	322	—	322	—	—	—	
312	315	306	310	—	305	—	—	
—	—	288	—	264	260	—	—	translation and rotation of VO_4 , VO_6
—	250	264	245	—	—	—	—	
—	215, 160, 130, 110, 75	—	210, 150	—	—	—	—	

Table 7. Frequencies (cm^{-1}) of maxima in vibrational spectra of MTa_2VO_9 ($M = \text{Dy, Ho, Er, Tm}$).

Dy		Ho		Er		Tm		Assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	
—	—	—	—	—	—	—	1010	stretching vibrations of VO_4 , TaO_6 , VO_6
—	—	—	—	—	985	—	—	
950(sh)	—	—	—	—	955	—	—	
—	—	—	—	—	930	—	—	
—	—	892	—	900	—	885	—	
—	—	—	890	—	895	—	—	
—	880	—	870	—	—	—	890	
—	—	—	—	—	855	—	—	
—	825	—	830	—	—	—	835	
820	—	824	—	—	845	840	—	
—	805	—	—	812	805	792	815	
—	—	—	760	—	785	—	—	
—	735	—	745	—	—	—	—	
—	—	—	730	—	—	—	—	
690	675	695	685	680	670	685	670	deformation vibrations of VO_4 , TaO_6 , VO_6
640	—	640	625	—	630	630	—	
590	600	590	605	592	580	—	—	
520	—	530	—	554	550	560(sh)	—	
—	—	—	510	—	505	—	—	
480(sh)	—	—	—	494	490	—	—	
—	480	—	—	—	—	—	485	
—	—	—	—	—	465	476	—	
430	440	430	—	—	455	—	—	
400(sh)	—	—	—	—	—	—	—	
—	375	—	—	—	—	—	385	
365	—	—	—	362	—	—	—	

Table 7 (continued).

Dy		Ho		Er		Tm		Assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	
325	315	325	330	—	—	—	—	} $\nu(\text{M}-\text{O})$
310	275	308	—	276	—	—	280	
260	255	250	—	—	—	—	250	
236	245	240	—	—	—	—	—	
224	220, 185, 175, 165, 115, 100, 80, 65	220	225, 205, 150	220	—	—	210, 170	} translation and rotation of VO_4 , VO_6

Table 8. Frequencies (cm^{-1}) of maxima in vibrational spectra of MTa_2VO_9 ($\text{M} = \text{Yb}$, Lu , Sc , Y).

Yb		Lu		Sc (IR)	Y		Assignment
IR	Raman	IR	Raman		IR	Raman	
—	1090	—	—	—	—	—	} stretching vibrations of VO_4 , TaO_6 , VO_6
—	1050	—	—	—	—	1045	
—	—	—	1020	—	—	1025	
—	—	—	1010	—	—	—	
—	—	—	—	990(sh)	—	—	
—	—	—	—	—	960(sh)	—	
—	—	—	930	910	—	910	
895	—	890	—	—	895	895	
—	900	—	890	—	—	885	
838	—	—	—	—	840	—	
—	815	—	835	—	—	830	
800	810	815	820	792	—	810	
—	—	—	790	—	—	—	
730(sh)	740	—	775	730(sh)	—	730	
—	—	—	765	—	—	—	
685	680	—	710	680(sh)	692	670	
—	—	—	665	630	640	640	
600	—	—	625	—	590	610	
560(sh)	—	—	—	574	535	—	} deformation vibrations of VO_4 , TaO_6 , VO_6
479	—	—	—	490	490	—	
—	480	—	455	—	—	485	
—	—	—	—	—	—	—	
—	—	450	—	—	430	450	
—	—	—	415	—	—	420	
385	—	—	370	—	—	375	
—	—	360	—	350	—	—	
—	—	—	315	296	—	—	} $\nu(\text{M}-\text{O})$
—	—	—	265	268	—	275	
255	—	—	255	—	—	255	
—	—	—	230	—	—	245	
—	—	—	—	—	—	230	} translation and rotation of VO_4 , VO_6
215, 175	—	—	210, 170, 150, 100, 65	—	—	200, 175, 95, 90, 75	

contains a group of intense lines in the region of $340\text{--}455\text{ cm}^{-1}$. Probably, resonance phenomena involving virtual states due to diffusion of laser light near the $^4\text{F}_{9/2}$ state of the Er^{3+} ion also occur in this case. Similar phenomena were reported for the $^7\text{F}_0$ state of the Eu^{3+} ion and the $^4\text{I}_{9/2}$ state of the Nd^{3+} ion in $\text{EuTa}_7\text{O}_{19}$ and LnTaO_4 crystals ($\text{Ln} = \text{Nd}$, Eu).¹³⁵

The empirical assignment of frequencies in the vibrational spectra of YTa_2VO_9 is based on the fact that its lattice contains almost regular VO_4 tetrahedra.^{136,137} The region of the stretching vibrations of these tetrahedra [$730\text{--}900\text{ cm}^{-1}$, cf. the assignment of the stretching vibration frequencies of VO_4 tetrahedra^{138,139} for the $[\text{VO}_4]^{3-}$ ion and for the $\text{Na}_3\text{M}(\text{VO}_4)_2$ compounds, where

$\text{M} = \text{Sc}$, Y , La – Lu] displays quite a few maxima (see Table 8), which may be due to vibrations of VO_4 groups linked through one oxygen atom.

The tantalates $\text{MTa}_7\text{O}_{19}$ ($\text{M} = \text{La}$, Ce) with the structures similar to that of YTa_2VO_9 are characterised by the presence of distorted TaO_6 octahedra. Probably, the structure of MTa_2VO_9 also contains distorted TaO_6 octahedra. The presence of vanadium-based polyhedra in the lattice of vanadatotantalates primarily results in variation of the frequencies originating from internal vibrations of the TaO_6 octahedra (ν and δ for $\text{Ta}-\text{O}$ and $\text{Ta}-\text{O}-\text{Ta}$) and in elongation of the bonds in the octahedra

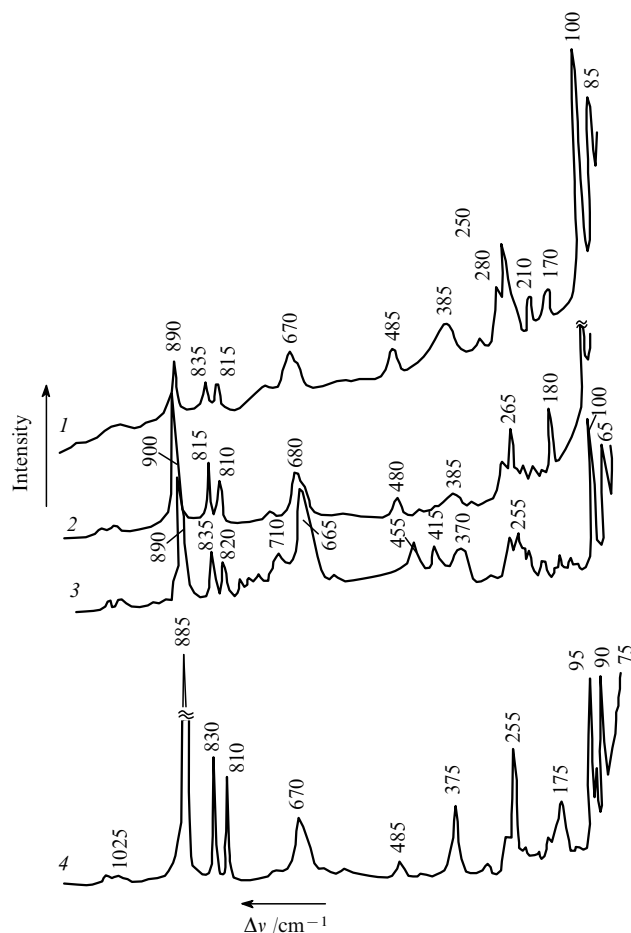


Figure 20. Raman spectra of MTa_2VO_9 , where $\text{M} = \text{Tm}$ (1), Yb (2), Lu (3), and the Raman spectrum of vanadatotantalate YTa_2VO_9 (4).

accompanied by a decrease in the vibration frequencies of the Ta–O terminal bonds.

Some frequencies in the spectra of YTa_2VO_9 were assigned to vibrations of distorted TaO_6 octahedra (see Table 8 and the frequency assignment in Refs 140 and 141). The spectra of orthovanadates MVO_4 and the assignment of the vibration frequencies of VO_4 tetrahedra have been documented.¹⁴² For example, the frequencies for YVO_4 are as follows: $\nu_1 = 888$, $\nu_2 = 376$, $\nu_3 = 836.8$, $\nu_4 = 487 \text{ cm}^{-1}$. Taking into account the line shapes in the Raman spectrum of the vanadatotantalate YTa_2VO_9 , some of the lines were assigned to the vibration frequencies of the VO_4 tetrahedron: $\nu_1 = 885$, $\nu_2 = 375$, $\nu_3 = 830$, $\nu_4 = 485 \text{ cm}^{-1}$. It is well known that for some tetrahedra, such as VO_4^{3-} , ReO_4^{3-} , FeO_4^{2-} , RuO_4^{2-} , FeO_4^{2-} ,¹⁴³ and for MTa_2VO_9 the frequency ν_3 is smaller than ν_1 .

2. MNb_2VO_9 crystals

The structures of MNb_2VO_9 crystals have not been determined. Tables 9–12 list the frequencies of the maxima in the vibration spectra of the vanadatoniobates MNb_2VO_9 ($\text{M} = \text{Sc}$, Y , La – Lu).⁹ The bands at 865 – 890 , 795 – 840 , 470 – 490 and 370 – 385 cm^{-1} can probably be assigned to the ν_1 , ν_3 , ν_4 and ν_2 vibrations of the VO_4 tetrahedra, respectively.

The bands in the IR spectra of these compounds differ in shapes and intensities. For vanadatoniobates of cerium subgroup lanthanides, comparatively intense medium-width bands at 200 – 600 cm^{-1} and one broad band at 600 – 1000 cm^{-1} are observed (Fig. 21). For instance, the NdNb_2VO_9 spectrum has some specific features: the band at 828 cm^{-1} is particularly intense. In the spectra of MNb_2VO_9 , where $\text{M} = \text{Ce}$, Pr , Sm , Eu , this band is less intense and is shifted from 828 cm^{-1} towards

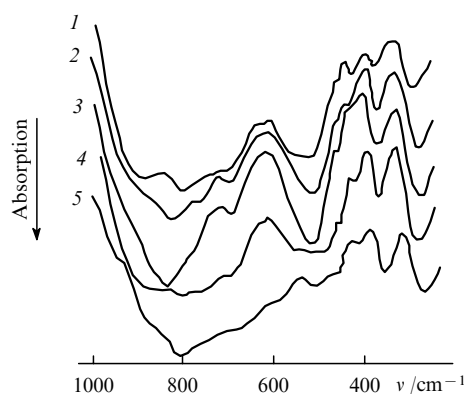


Figure 21. IR spectra of MNb_2VO_9 , where $\text{M} = \text{Ce}$ (1), Pr (2), Nd (3), Sm (4), Eu (5).

higher or lower frequencies. Such frequency shifts are less pronounced in the deformation vibration region. The IR spectra of yttrium subgroup compounds are similar: the frequency region characteristic of deformation vibrations displays comparatively intense medium-width bands; the stretching vibration bands merge into one broad band (Figs 22, 23). It should be noted that the IR spectra of LaNb_2VO_9 (Fig. 24, spectrum 1) and vanadatoniobates of yttrium subgroup elements are similar to the spectra of vanadatoniobates of cerium subgroup elements. The spectra of YNb_2VO_9 and ScNb_2VO_9 (Fig. 24, spectra 2, 3) mainly differ in the intensity of the absorption bands. It is noteworthy that for compounds with $\text{M} = \text{Gd}$, Tb , Dy , Ho the broad band in the region of deformation vibrations splits into two narrow bands at

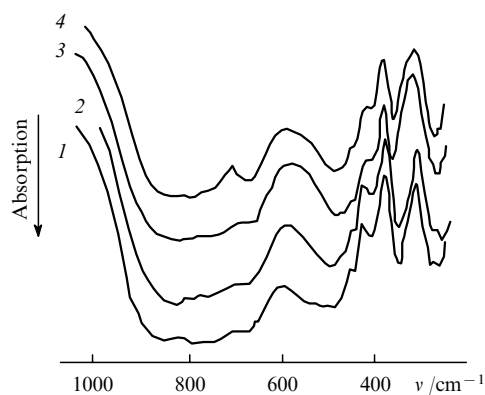


Figure 22. IR spectra of MNb_2VO_9 , where $\text{M} = \text{Gd}$ (1), Tb (2), Dy (3), Ho (4).

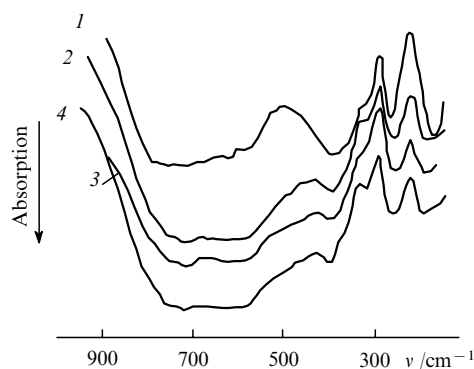


Figure 23. IR spectra of MNb_2VO_9 , where $\text{M} = \text{Er}$ (1), Tm (2), Yb (3), Lu (4).

Table 9. Frequencies (cm^{-1}) of maxima in vibrational spectra of MNb_2VO_9 ($M = \text{La, Ce, Pr, Nd}$).

La		Ce (IR)	Pr		Nd		Assignment
IR	Raman		IR	Raman	IR	Raman	
—	—	—	—	—	—	1070	} stretching vibrations of VO_4 , TaO_6 , VO_6
—	1000	—	—	—	—	—	
—	—	—	—	990	—	—	
885	910	—	—	—	—	—	
865	—	875	—	—	—	—	
—	850	—	—	855	—	—	
850	—	—	—	—	—	—	
816	—	—	820	—	828	—	
800	—	800	—	—	—	—	
—	—	—	—	795	—	—	
—	—	—	—	785	—	—	
775	—	—	760	—	770	—	
—	—	690	690	—	684	—	
675	670	—	—	670	—	—	
—	—	630–620	620–615	—	625–620	—	
—	610	—	—	610	—	—	
—	—	560	—	—	—	—	} deformation vibrations of NbO_n , VO_4 , VO_6
—	—	510	510	—	508	—	
495	—	—	—	—	—	—	
—	470	—	—	480	—	—	
—	—	—	—	—	—	—	
—	—	450	450	—	450	—	
430	—	—	—	—	—	—	
—	—	420	420	—	420	—	
—	370	—	—	370	—	—	
—	—	365	365	—	360	—	
—	340	—	—	—	—	310	
—	—	280	276	—	286	—	} $\nu(\text{M}-\text{O})$
270	—	—	—	255	—	—	
210, 150, 115	—	—	—	220, 175, 135, 125, 100	—	185	} translation and rotation of VO_4 , VO_6
—	—	—	—	—	—	—	

Table 10. Frequencies (cm^{-1}) of maxima in vibrational spectra of MNb_2VO_9 ($M = \text{Sm, Eu, Gd, Tb}$).

Sm		Eu (IR)	Gd		Tb		Assignment
IR	Raman		IR	Raman	IR	Raman	
—	990	—	—	—	—	1000	} stretching vibrations of NbO_n , VO_4 , VO_6
—	935	—	—	—	—	—	
—	885	—	—	—	880	890	
—	870	—	870	880	—	—	
860	—	—	—	—	—	—	
—	830	—	—	820	—	840	
—	—	—	—	—	840	—	
—	810	—	810	—	—	810	
800	—	803	—	—	—	—	
760	—	—	770	—	—	770	
690	680	670	690–670	685	685–670	670	} deformation vibrations of NbO_n , VO_4 , VO_6
620	620	590	—	610	—	620	
550	—	—	—	—	—	—	
510–480	—	506–467	505	—	510	—	
—	490	—	—	—	—	—	
—	470	—	475	—	480	—	
450	—	450	460	—	455	—	
—	—	—	420	420	—	420	
415	—	412	—	—	415	—	
—	370	—	—	—	—	385	
365	—	—	360	—	360	—	} translation and rotation of VO_4 , VO_6
—	350	352	—	—	—	—	

Table 10 (continued).

Sm		Eu (IR)	Gd		Tb		Assignment
IR	Raman		IR	Raman	IR	Raman	
—	—	—	290	—	290	—	} $\nu(\text{M}-\text{O})$
270	—	268	270	—	260	270	
	255		—	260		—	
	210, 175, 150		170	210, 170, 115		175, 110	translation and rotation of VO_4 , VO_6

Table 11. Frequencies (cm^{-1}) of maxima in vibrational spectra of MNb_2VO_9 ($\text{M} = \text{Dy, Ho, Er, Tm}$).

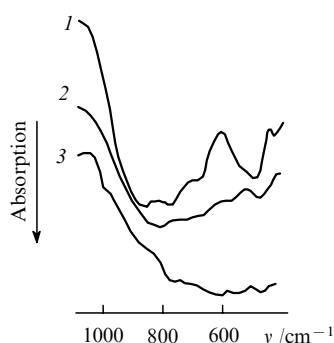
Dy		Ho		Er		Tm (IR)	Assignment
IR	Raman	IR	Raman	IR	Raman		
—	1050	—	—	—	—	—	} stretching vibrations of NbO_n , VO_4 , VO_6
—	—	—	—	—	940	—	
—	—	—	—	—	—	907	
—	—	—	—	890	—	—	
—	880	—	—	—	—	—	
—	—	860	—	865	—	—	
—	—	—	—	—	—	850	
840	—	840	—	—	—	—	
—	815	—	—	—	—	—	
810	805	810	—	805	—	810	
—	—	780	—	775	—	—	
—	—	—	—	—	—	740	
—	—	—	—	725	—	—	
—	—	690	690	680	—	685	
—	—	—	650	—	—	—	
—	620	—	—	620	—	—	} deformation vibrations of NbO_n , VO_4 , VO_6
—	—	—	—	—	605	—	
—	—	—	590	—	595	—	
—	—	—	—	—	550	—	
—	—	—	540	—	545	545	
—	—	—	—	—	510	—	
495	—	500	505	500	—	—	
475	—	485	—	480	—	488	
—	480	—	—	—	—	—	
455	—	455	—	455	—	455	
—	—	—	430	—	440	—	
415	—	420	—	415	—	414	
—	—	—	405	—	—	—	
—	—	—	390	—	—	—	
—	370	—	—	—	—	—	} $\nu(\text{M}-\text{O})$
370	—	370	370	365	—	—	
—	—	—	—	—	—	356	
—	—	—	300	290	—	—	
270	265	270	—	270	—	280	
	—		—		260	—	translation and rotation of VO_4 , VO_6
	220, 150, 115		230, 175		175, 125, 90		

260–270 cm^{-1} . This can be due to distortion of the polyhedra formed by the M^{3+} ions ($\text{M} = \text{Gd, Tb, Dy, Ho}$). The positions of certain bands depend on the nature of the M^{3+} cation: the decrease in the ionic radii in the Ce^{3+} – Lu^{3+} series is accompanied by a shift of the band at 420 cm^{-1} to 412 cm^{-1} (Ho^{3+} is an exception). This may originate from an increase in the covalency of the bond of the lanthanide with the environment and enhancement of the crystal field effect as the M^{3+} ionic radius decreases. The Raman spectra could be recorded only for the compounds with $\text{M} = \text{La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er}$; only the most intense lines were recorded for NdNb_2VO_9 . In the spectra of lanthanum, praseodymium, samarium and gadolinium vanada-

toniobates, the most intense narrow band is shifted from 850 to 880 cm^{-1} (Fig. 25). Similarly, the decrease in ionic radius in the series La^{3+} , Pr^{3+} , Sm^{3+} , Gd^{3+} results in displacement of the relatively broad band at 670 cm^{-1} to 685 cm^{-1} . The pair of lines at 650 and 690 cm^{-1} in the spectrum of HoNb_2VO_9 has the highest intensity (Fig. 26, spectrum 2). This is probably due to the resonance enhancement of the Raman spectrum upon helium–neon laser excitation of the holmium ion near the $^5\text{F}_5$ state. The enhancement of the line at 940 cm^{-1} occurs due to resonance effects, viz., laser light scattering near the $^4\text{F}_{9/2}$ state of the erbium ion in ErNb_2VO_9 . The bands at 850–880 and 670–690 cm^{-1} in the spectra of vanadatoniobates, like those in the case of vanada-

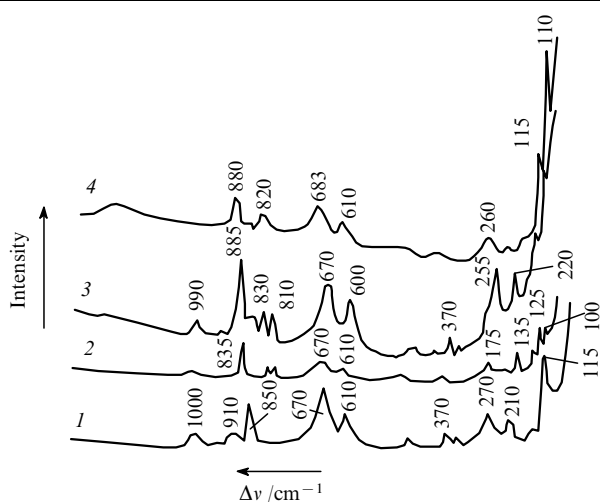
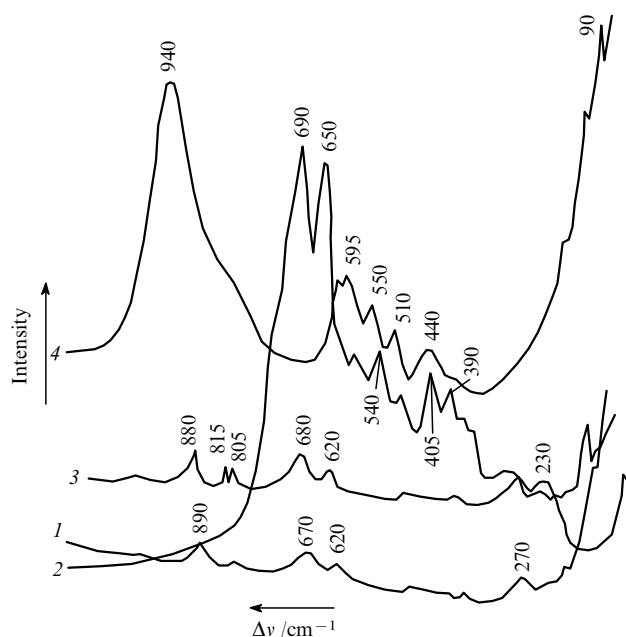
Table 12. Frequencies (cm^{-1}) of maxima in vibrational spectra of MNb_2VO_9 ($\text{M} = \text{Yb, Lu, Sc, Y}$).

Yb	Lu	Sc	Assignment	Y	Assignment
—	—	990	stretching vibrations of NbO_m , VO_4 , VO_6 , $\text{V}-\text{O}-\text{V}$	990	stretching vibration of NbO_m
895	900	—		—	—
850	850	850		—	—
810	810	—		—	—
—	—	765		810	stretching vibration of VO_4
730	730	—	deformation vibrations of NbO_m	—	—
685	685	—		665, 575	deformation vibrations of NbO_m
—	—	—		—	—
—	—	615		—	—
—	550	555		470	$\nu_4(\text{VO}_4)$
490	488	—	deformation vibrations of VO_4 , VO_6	—	—
455	455	475		—	—
415	412	—		—	—
350	352	—		—	—
280	285	—	$\nu(\text{M}-\text{O})$	—	—

**Figure 24.** IR spectra of MNb_2VO_9 , where $\text{M} = \text{La}$ (1), Y (2), Sc (3).

totantalates, originate from the stretching vibrations of the $\text{Nb}-\text{O}$ bonds involving the $\text{M}-\text{O}$ bonds.

NMR data were used for empirical assignment of certain frequencies in the vibrational spectra of MNb_2VO_9 . In the vanadatonibate YNb_2VO_9 , vanadium occupies two non-equivalent regular tetrahedral positions; the vanadium environment in one of them coincides with the tetrahedral environment of

**Figure 25.** Raman spectra of MNb_2VO_9 , where $\text{M} = \text{La}$ (1), Pr (2), Sm (3), Gd (4).**Figure 26.** Raman spectra of MNb_2VO_9 , where $\text{M} = \text{Tb}$ (1), Ho (2), Dy (3), Er (4).

vanadium in the vanadatotantalate YT_2VO_9 . In ScNb_2VO_9 crystals, vanadium occupies two non-equivalent crystallographic positions: one position corresponds to a distorted octahedral environment while the other corresponds to a slightly distorted tetrahedral environment; the type of the VO_4 tetrahedra in ScNb_2VO_9 is similar to one of the types of tetrahedron in YNb_2VO_9 . The YNb_2VO_9 and YT_2VO_9 compounds have different structures. On the other hand, YNb_2VO_9 and ScNb_2VO_9 have niobium-formed polyhedra of the same symmetries.

The IR and Raman spectra of the vanadatonibates MNb_2VO_9 , where $\text{M} = \text{Sc, Y, La}$, are virtually similar and mostly differ in the band intensities. Therefore, the structures of MNb_2VO_9 are likely to contain the same set of polyhedra, namely VO_4 , VO_6 and NbO_m ; the structural difference between these compounds is that the polyhedra in the lattices of MNb_2VO_9 crystals are connected in different ways. The existence of vanadium polyhedra in YNb_2VO_9 and ScNb_2VO_9 was established reliably; probable assignment of bands in the IR spectra of these compounds was made on this basis (see Table 12).^{138, 140, 144, 145}

The majority of lines in the Raman spectra of MNb_2VO_9 are broadened. This implies that the lattice atoms occupy non-equivalent crystallographic positions and form several types of similar polyhedra with different symmetries. The lines in the Raman spectra of MT_2VO_9 crystals are less broadened, hence the MT_2VO_9 structure has fewer non-equivalent atomic positions.

As in the case of vanadatotantalates, certain frequencies in the Raman spectra of vanadatonibates were assigned based on the intensities, shapes and positions of particular lines. Comparison of these data with those for MVO_4 orthovanadates (see Refs 146, 147) resulted in the assignment given in Tables 9–12 ($\nu_3 < \nu_1$, as in the case of MT_2VO_9).

The changes in the ν_1 and ν_3 frequencies in the Raman spectra of MT_2VO_9 and MNb_2VO_9 polycrystals were analysed (see Ref. 9). The spectral lines are sufficiently narrow, hence it is quite reasonable to construct various functional dependences for them. Figure 27 presents the dependences of the ν_1 and ν_3 frequencies in the Raman spectra of LnTa_2VO_9 and LnNb_2VO_9 on the atomic number (z) and the ionic radius (r_{Ln}) of Ln^{3+} (the ionic radii were taken from Ref. 134). The ν_1 frequency is given only for LnTa_2VO_9 crystals. Figure 27a clearly shows the scatter of experimental points near the straight line drawn using the least-

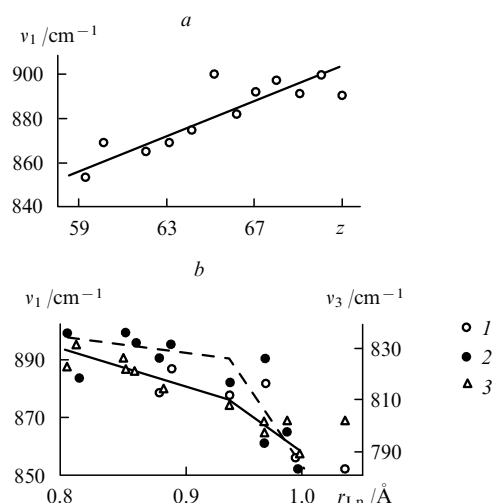


Figure 27. Dependence of vibration frequencies ν_1 and ν_3 of VO_4 tetrahedra on the atomic number in LnTa_2VO_9 (a) and the Ln^{3+} ionic radius in LnTa_2VO_9 (1, 2) and LnNb_2VO_9 (3) (b). The experimental points refer to the frequencies ν_1 (1, 3) and ν_3 (2); the calculated curves are drawn for the frequencies ν_1 (solid line) and ν_3 (dashed line).

squares method. The ν_1 frequency for the LnTa_2VO_9 compounds increases as the lanthanide atomic number changes in the series Pr–Lu. This phenomenon can be explained by the lanthanide contraction. The scatter of ν_1 values around the straight line is different for different lanthanides. The greatest deviations are observed for Tb, Nd and Lu. It is well known that non-uniform spreading of f orbitals, which depends on z and originates from spin-orbital coupling, is superimposed on the lanthanide contraction.¹¹ This effect might explain the scatter of ν_1 for the compounds under consideration. Figure 27b shows the same kind of scatter of experimental data and an increase in ν_1 and ν_3 with a decrease in the Ln ionic radius; in addition, the straight lines have sharp breaks around $r_{\text{Ln}} = 0.094$ nm (the ionic radius of Gd^{3+}). The dependences of other properties in the series of f elements are also characterised by similar breaks.¹¹ As shown by Muck *et al.*,¹⁴⁸ the $\nu_1(\text{VO}_4)$ frequency in the IR spectra of $\text{Y}(\text{PO}_4)_x(\text{VO}_4)_{1-x}$ mixed crystals increases as x changes from 0 to 0.7. This can be due to the effect on the bond vibrations in VO_4 tetrahedra exerted, for example, by other VO_4 groups.

3. LaTaB_2O_7 , $\text{La}_4\text{VBO}_{10}$, $\text{Ln}_7\text{V}_2\text{BO}_{17}$ crystals and solid solutions based on them

Table 13 lists the frequencies of maxima in the vibrational spectra of solid solutions based on LaTaB_2O_7 . The bands in the regions of 718–720 and 610–620 cm^{-1} can probably be assigned to the ν_2 and ν_4 vibrations of the BO_3 triangles. Frequencies up to

Table 13. Frequencies (cm^{-1}) of maxima in vibrational spectra of $\text{La}_{1-x}\text{Sm}_x\text{TaB}_2\text{O}_7$.

x						Assignment
0	0 ^a	0.001	0.01	0.05	0.1	
	155, 179, 215, 267					
300	—	300	300	300	300	} $\nu(\text{La}-\text{O}), \nu(\text{O}-\text{B}-\text{O}), \nu(\text{O}-\text{Ta}-\text{O})$
315	—	310	311	310	310	
—	321	320	325	321	320	
350	—	—	352	352	352	
375	370	372	370	372	370	
386	—	390	390	390	390	
400	—	425	423	425	427	
492	—	493	490	490	493	
525(sh)	—	525	525	525	525	
540	536	540	540	540	542	
560	564	557	560	557	562	} deformation vibrations of BO_3 ; stretching vibrations of TaO_n
580	—	577	580	570	581	
590	—	—	—	595	—	
614	620	615	615	610	615	
667	—	—	665	665	667	} stretching vibrations of TaO_n
677	—	675	675	673	677	
—	700	—	—	—	—	
—	—	718	—	720	720	
—	749	—	—	—	—	} stretching vibrations of TaO_n
765	775	764	765	775	768	
802	—	802	802	802	805	
895	—	890	890	890	890	
923	920	920	920	—	900	
960	958	960	960	960	965	
1029	—	1026	1027	1030	1030	
—	1045	—	—	—	1050	} stretching vibrations of BO_3
1085	—	1085	1085	1085	1090	
—	—	—	—	1160	—	
1170	—	1165	1165	1170	1170	
1187	—	—	—	—	—	}
—	—	—	1230	1230	—	

Table 13 (continued).

<i>x</i>						Assignment
0	0 ^a	0.001	0.01	0.05	0.1	
1235	—	1235	1240	—	1240	} stretching vibrations of BO ₃
—	1250	—	—	—	—	
1270	—	1270	1275	1272	1275	
—	—	1293	1295	1300	1300	
—	1316	—	—	—	—	
—	1412	—	—	—	—	

^a Raman spectroscopy data.**Table 14.** Frequencies (cm⁻¹) of maxima in vibrational spectra of La_{4(1-x)}Ln_{4x}VBO₁₀ (Ln = Eu, Sm).

<i>x</i>					Assignment	<i>x</i>					Assignment
0	0.01(Eu)	0.05(Eu)	0.05(Sm)	0.01(Sm) ^a		0	0.01(Eu)	0.05(Eu)	0.05(Sm)	0.01(Sm) ^a	
—	—	—	—	—	175 translation and rotation of VO ₄	—	—	—	—	850	} stretching vibrations of VO ₄ , V—O—V
—	—	—	425	—	275, 395 } $\nu(\text{L—O})$, $\nu(\text{O—B—O})$	865	864	860	860	—	
445	440	440	445	—		890	885	885	883	—	
486	482	480	485	—		906	—	—	—	905	
515	515	510	510	505		927	928	928	925	—	
—	575	—	—	—		945	941	942	941	—	
593	594	594	592	—	} $\nu_4(\text{BO}_3)$	—	—	—	975	—	
613	612	612	612	—		1000	1000	1000	—	—	
715	718	715	717	—	} $\nu_2(\text{BO}_3)$	1025	1025	1025	1025	—	
748	746	740	745	—		1080	1080	1080	1080	—	
—	—	—	760	—		1120	1120	1120	1120	—	
780	775	775	775	—	} stretching vibrations of VO ₄ , V—O—V	1135	1135	1135	1135	—	
800	795	800	795	—		1145	1145	1145	1145	—	
832	830	828	829	830		1180	1180	1180	1180	—	
—	—	—	—	—		1250	1242	1245	1245	—	
—	—	—	—	—		1280	1275	1275	1276	—	

^a Raman spectroscopy data.

1000–1100 cm⁻¹ correspond to the fundamental lattice vibrations of the simple rare-earth element tantalates (see Ref. 141). The vibrations of the B—O bonds occur in the region up to 1400 cm⁻¹ (see Ref. 149). Thus, the frequencies in the region of 1170–1412 cm⁻¹ in mixed-anion crystals probably correspond to vibrations of the B—O bonds in BO₃. The bands in the region of 155–1100 cm⁻¹ belong to the vibrations of groups containing tantalum, boron and lanthanum. The bands at 1170–1270 cm⁻¹ probably arise from ν_3 antisymmetric stretching vibrations of isolated BO₃ triangles.

It is well known that the isolated BO₃³⁻ anion is characterised by vibrations in the region of 1100–1300 (degenerate antisymmetric stretching vibration) and 700–900 cm⁻¹ (nonplanar degenerate deformation vibration). The reduction of boron symmetry in the case of LaBO₃ or the L-modification of SmBO₃ causes the frequency of 940 cm⁻¹ to appear, which corresponds to symmetric stretching vibrations.^{150, 151} Association of anions in rings or chains distorts their structures, which leads to broadening and splitting of bands, overlap of regions of different vibrations and often to a high-frequency shift of the stretching vibration bands. The character and span of frequencies of this group of vibrations in the IR spectra of La_{1-x}Sm_xTaB₂O₇ is not inconsistent with association of borate anions in rings and chains. Comparison of the spectra presented here with the results obtained for REE tantalates provides a reason to assume that the frequencies 600–830 cm⁻¹ include the stretching vibrations of TaO_n polyhedra in addition to the deformation vibrations of the BO₃ groups, whereas vibrations at 200–500 cm⁻¹ can be due to various deformation modes of O—B—O and O—Ta—O. The

Raman spectrum of the boratotantalate LaTaB₂O₇ contains a dominant line with $\nu = 370$ cm⁻¹ (Fig. 28 a). The presence of an intense line in the region of 370–430 cm⁻¹ of the Raman spectrum is characteristic of REE tantalates and comes from the deformation vibration of O—Ta—O.

The IR spectra of La_{1-x}Sm_xTaB₂O₇ solid solutions lack certain frequencies that are present in the spectra of LaTaB₂O₇ (Fig. 28 b); in addition, a series of frequencies appears (see Table 13). This means that replacement of lanthanum ions with samarium ions results in deformation of lattice polyhedra in solid solutions. This probably changes the selection rule of the vibrations. The same is true for the vibrational spectra of La_{1-x}Eu_xTaB₂O₇ solid solutions (see Ref. 152). Table 14 presents the frequencies of maxima in the vibrational spectra of La_{4(1-x)}Ln_{4x}VBO₁₀ solid solutions (Ln = Sm, Eu). According to NMR data, the lattices of the crystals indicated above contain almost regular VO₄ tetrahedra which have one common oxygen atom with the adjacent VO₄ tetrahedra. The IR spectra of the pure compound and its solid solutions are characterised by the presence of three intense absorption bands at 400–600, 650–950 and 1150–1350 cm⁻¹ (see Ref. 153). The spectra of solid solutions lack some frequencies and contain some new frequencies in comparison with the spectrum of La₄VBO₁₀ (Fig. 29 a).

The bands in the region of 480–486 cm⁻¹ can be assigned to the ν_4 vibrations of the VO₄ tetrahedra, while those in the regions of 1275–1280, 941–945, 715–748 and 592–621 cm⁻¹, to the ν_3 , ν_1 , ν_2 and ν_4 vibrations of the BO₃ triangles, respectively.

The Raman spectrum of the (La_{0.09}Sm_{0.01})₄VBO₁₀ solid solution contains five high-intensity lines (Fig. 29 b) and two

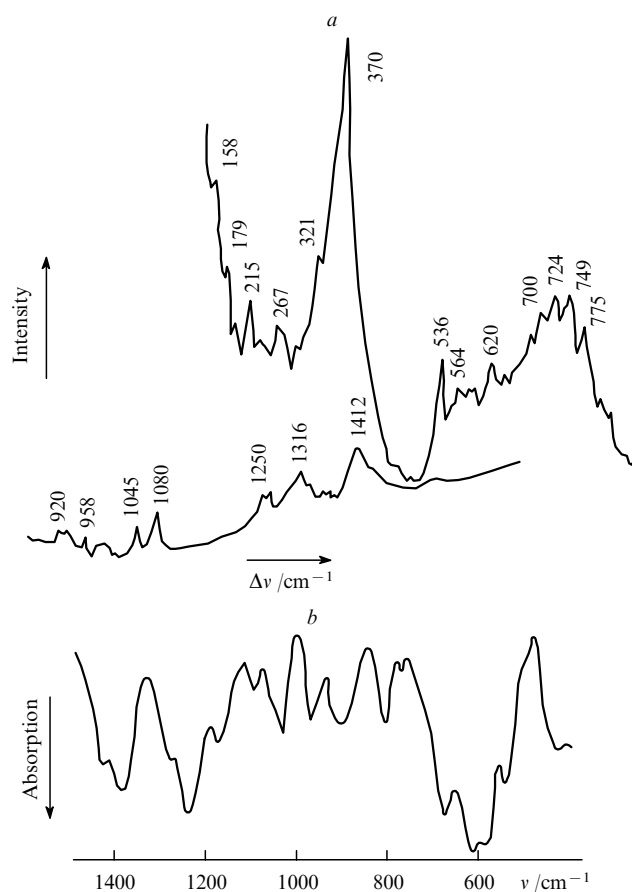


Figure 28. Vibrational spectra of LaTaB_2O_7 . (a) Raman spectrum; (b) IR spectrum.

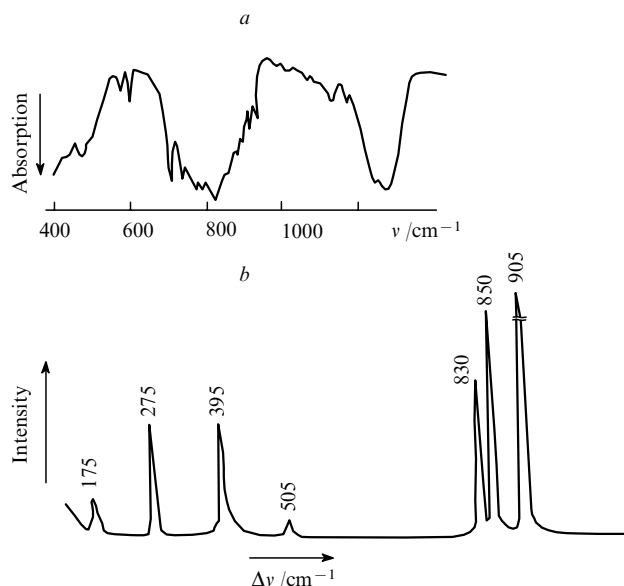


Figure 29. IR spectrum of $\text{La}_4\text{VBO}_{10}$ (a) and Raman spectrum of $(\text{La}_{0.99}\text{Sm}_{0.01})_4\text{VBO}_{10}$ (b).

medium-intensity lines. Using the data for the vibration frequencies of BO_3 groups (see Refs 138, 150), a series of IR bands were assigned to the vibrations of BO_3 borate triangles (see Table 14). It follows from the assignment presented in Table 14 that $\text{La}_4\text{VBO}_{10}$ is a mixed-anion compound. Probably, the La—O

bond in the complex borates in question is essentially ionic, as shown for $\text{LaMgB}_5\text{O}_{10}$, LaBO_3 , etc.¹⁵⁴

The IR spectra of $\text{Ln}_7\text{V}_2\text{BO}_{17}$ contain bands ascribed to deformed BO_3 groups;¹²⁷ in particular, at 1172, 1215, 1310 and 1350 cm^{-1} for $\text{Ln} = \text{Nd}$.

* * *

Thus, the possibility of formation of ternary oxide compounds in ternary oxide systems of Group III and VB elements depends both on the ratio of the ionic radii of elements in the anionic part of the compound and on the cation radius. The vibrations of complex anionic groups in ternary oxide crystals can be interpreted as vibrations of quasi-isolated polyhedra, such as VO_4 , VO_6 and RO_n , and BO_3 triangles. The chemical bonds of solid solutions with complex anions involve the f orbitals, as is evident from the lattice dynamics of these objects. As a rule, ternary compounds decompose to binary ones on heating. This is also characteristic of ternary compounds of other Groups of the Periodic Table. For example, titanoniobates and -tantalates, $\text{LnTiNb}(\text{Ta})\text{O}_6$, undergo peritectic decomposition to give rutile and the corresponding niobates and tantalates, $\text{LnNb}(\text{Ta})\text{O}_4$.¹³ The decomposition products of compounds with mixed cations, e.g., $\text{Ln}_2\text{Ca}_3(\text{BO}_3)_4$ or $\text{LnAl}_3(\text{BO}_3)_4$, contain double borates, viz., LnBO_3 and AlBO_3 .⁶⁶

The data presented in this review can serve as a basis for studies of more complex multicomponent oxide systems, e.g., $\text{M}_2\text{O}_3 - \text{V}_2\text{O}_5 - \text{Nb}_2\text{O}_5 - \text{Ta}_2\text{O}_5$, $\text{M}_2\text{O}_3 - \text{M}'_2\text{O}_3 - \text{V}_2\text{O}_5 - \text{Nb}_2\text{O}_5 - \text{Ta}_2\text{O}_5$, etc. The use of spectroscopic methods allows one to understand the regularities of the formation of phases and their structures in the systems under consideration.

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^c — *Moscow Univ. Bull. (Engl. Transl.)*

^d — *Russ. J. Inorg. Chem. (Engl. Transl.)*

^e — *Russ. J. Coord. Chem. (Engl. Transl.)*

^f — *Russ. J. Appl. Spectrosc. (Engl. Transl.)*

^g — *Russ. J. Phys. Chem. (Engl. Transl.)*

Synthesis of insect pheromones belonging to the group of (Z)-trisubstituted alkenes

N Ya Grigorieva, P G Tsiklauri

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Abstract. Stereo- and regiocontrolled methods for the construction of a (Z)-trisubstituted C=C bond and for the regiospecific introduction of a chiral fragment are exemplified in total syntheses of insect pheromones belonging to (Z)-trisubstituted alkenes. The bibliography includes 113 references.

I. Introduction

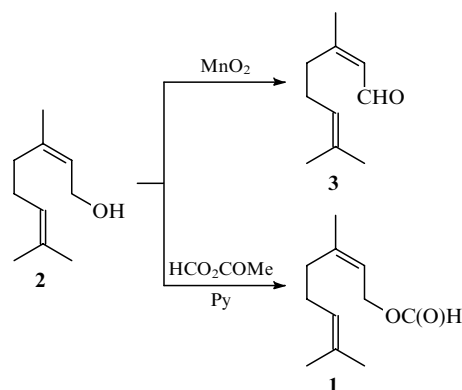
In the last two decades, it was found that the biological activities of a series of important natural compounds, such as low-molecular-weight bioregulators, viz., polyprenols, dolichols, antibiotics of a strobilurin family and pheromones of different species of insects, are associated with the presence of a (Z)-trisubstituted alkene fragment in these molecules. In this connection, the problem of the regio- and stereocontrolled synthesis of (Z)-trisubstituted alkenes is of substantial methodological and practical interest. A rather small group of insect pheromones containing this structural fragment represents a 'proving ground' for the elucidation of the synthetic potential of methods developed for the formation of (Z)-trisubstituted C=C bonds. In the total syntheses of these pheromones, all known procedures for the stereoselective construction of (Z)-trisubstituted alkenes were employed. These methods can find use in the preparation of other biologically active compounds. In addition, the approaches developed for the formation of chiral centres are also of obvious interest.

In the present review, methods for the regio- and stereocontrolled construction of (Z)-trisubstituted C=C bonds and the regiospecific introduction of a chiral centre, which are of importance for organic synthesis, are exemplified in total syntheses of pheromones of the above-mentioned group.

We believe that the solution of this problem calls for systematisation of the available data on the syntheses of the target structures, which are ranked in the order of increasing difficulty. Attention will be focussed on procedures for the construction of (Z)-trisubstituted alkene fragments and methods for the formation of chiral centres.

II. Synthesis of the alarm pheromones of the mold mite *Tyrophagus putrescentiae*, the astigmatid mite *Glycyphagus domesticus* and the ant *Oecophylla longinoda*

In the late 1970s, Kuwahara *et al.*^{1,2} demonstrated that neryl formate (**1**) is the alarm pheromone of one of the major pests of cereal crops, viz., the mold mite *Tyrophagus putrescentiae*. Later,³ this conclusion was confirmed by bioassays of synthetic neryl formate (**1**) prepared from nerol (**2**).



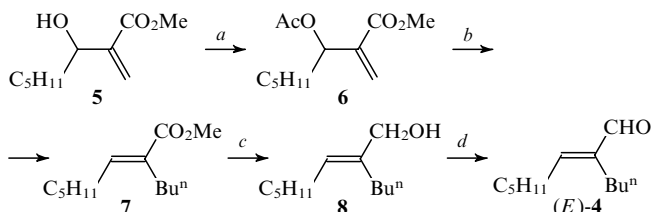
Later, Kuwahara and Koshii⁴ have found that neral (**3**), which can also be readily prepared from nerol (**2**), is the alarm pheromone of the astigmatid mite *Glycyphagus domesticus*.

α,β -Unsaturated aldehyde **4**, which is a hexanal dimerisation product, was isolated by Baker and coworkers in 1975.⁵ This is the alarm pheromone of the African weaver ant *Oecophylla longinoda*. Although, in strict accordance with the IUPAC nomenclature, aldehyde **4** is the (E)-isomer, the carbon substituents at the C=C bond are in *cis* positions with respect to each other. Disubstituted α,β -unsaturated aldehydes of this type are precursors of (Z)-methylalkenes. Hence, we believe that it is reasonable to consider the synthesis of the aldehyde **4** in the present review. In 1966, Basavaian and Hyma⁶ synthesised the aldehyde **4** with the use of the Baylis–Hillman reaction⁷ for the regio- and stereoselective construction of its trisubstituted alkene fragment.

Hydroxy ester **5**, which was prepared by the condensation of hexanal with methyl acrylate under conditions proposed by Baylis and Hillman,⁷ was converted into acetate **6**. The reaction of the latter with PrMgBr afforded ester **7** as the only product. Reduction of the ester group and oxidation of the resulting alcohol **8**

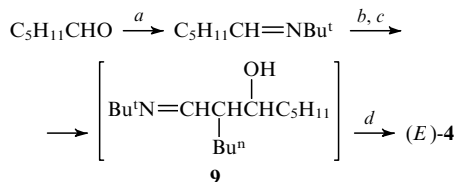
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with pyridinium chlorochromate gave rise to the aldehyde **4** (the overall yield was 20.5%).



(a) AcCl, Py; (b) Pr^nMgBr ; (c) Bu_2^iAlH ; (d) PCC (pyridinium chlorochromate), CH_2Cl_2 .

A simpler yet highly stereoselective procedure for the synthesis of the aldehyde **4**⁸ involves condensation of *N*-*tert*-butylhexanimine with hexanal yielding β -hydroxy imine **9**. Acid scission of the latter afforded thermodynamically more favourable⁹ aldehyde (*E*)-**4** in 70% yield (the stereoselectivity was ~ 98%). The aldehyde (*E*)-**4** was also identified by Baker *et al.*¹⁰ as a component of the alarm pheromone of the beetle *Amblypelta nitida*.



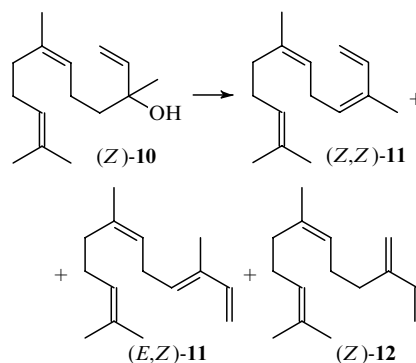
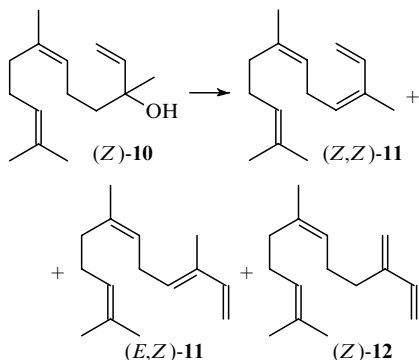
(a) Bu^tNH_2 ; (b) LDA (lithium diisopropylamide); (c) $\text{C}_5\text{H}_{11}\text{CHO}$; (d) H_3O^+ .

III. Syntheses of ant trail pheromones

1. Trail pheromones of the fire ant *Solenopsis invicta*

As early as 1959, Wilson¹¹ demonstrated that fire ants produce a special trail pheromone, which allows members of the community to find routes to sources of food, new areas, *etc.*

Van der Meer and coworkers¹² isolated this pheromone, established that it represents a mixture of at least five closely related compounds and separated these compounds by preparative GLC. Based on the results of studies of the physicochemical properties of individual components of this mixture, two compounds were assigned to the α -farnesene series and one compound was assigned to the allofarnesene series. The configurations of the pheromone components were established by comparing the spectral data (UV, ^1H NMR and mass spectra) of natural and authentic samples of α - and allofarnesenes synthesised in an unequivocal way. Thus dehydration of (*Z*)-nerolidol **10** in a POCl_3 -Py system at 160 °C afforded a mixture of isomeric α -farnesenes, (*Z,Z*)- and (*E,Z*)-**11**, and (*Z*)- β -farnesene, (*Z*)-**12**. Dehydration of the isomer (*E*)-**10** under the same conditions gave rise to a mixture of (*E,E*)- and (*Z,E*)- α -farnesenes (**11**) and (*E*)- β -farnesene [(*E*)-**12**].¹²

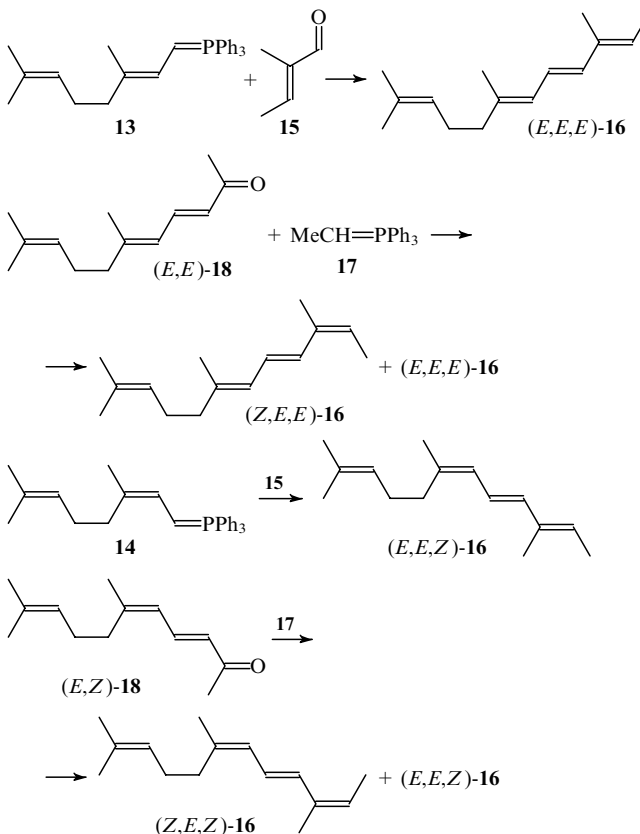


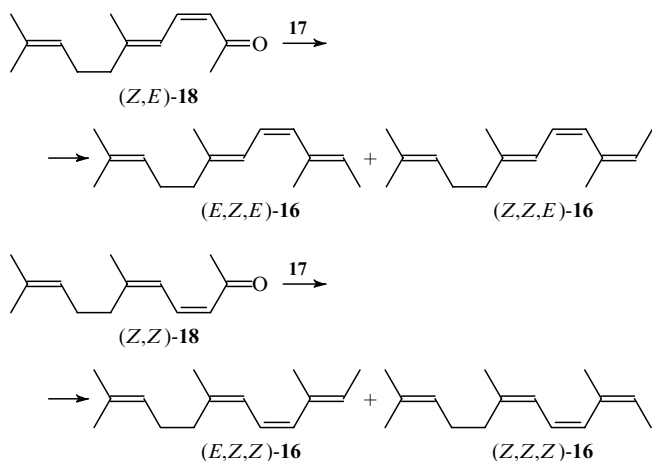
Based on comparison of the physicochemical characteristics of farnesenes **11** and the components of the fire ant trail pheromone, it was reliably established that the major component of this pheromone has the structure (*Z,E*)-**11** and one of the minor components has the structure (*E,E*)-**11**. It should be noted that α -farnesene (*Z,E*)-**11** was identified as a component of trail pheromones also of other ant species.¹³

With the aim of establishing the stereochemistry of the components of the fire ant trail pheromone belonging to the allofarnesene series, all eight possible isomeric allofarnesenes were synthesised using the Wittig reaction.¹⁴

It appeared that the condensation of ylides **13** and **14** generated from geranyl- and nerylphosphonium bromides, respectively, with tiglic aldehyde (**15**) proceeded stereoselectively to form allofarnesenes (*E,E,E*)-**16** and (*E,E,Z*)-**16**, respectively. To the contrary, the condensation of triphenylphosphonium ethylide **17** with isomeric pseudoionones (*E,E*)-**18** or (*E,Z*)-**18** was non-stereoselective.

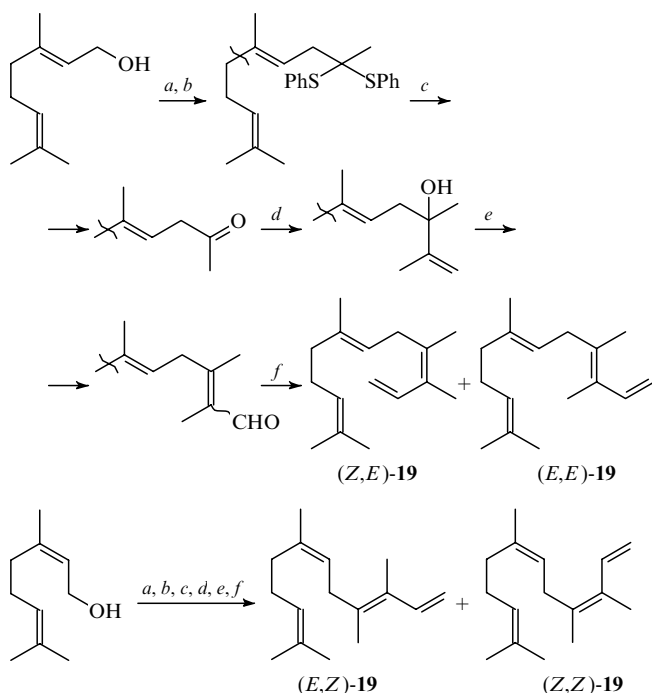
The reaction of the isomer (*E,E*)-**18** afforded a mixture of (*E,E,E*)- and (*Z,E,E*)-**16**, whereas the isomer (*E,Z*)-**18** gave a mixture of (*E,E,Z*)- and (*Z,E,Z*)-**16**. The condensation of the (*Z,E*)-pseudoionone, (*Z,E*)-**18**, with the ylide **17** yielded a mixture of (*E,Z,E*)-**16** and (*Z,Z,E*)-**16**, whereas the reaction of the





(Z,Z)-pseudoionone [(Z,Z)-18] with the ylide **17** afforded a mixture of (E,Z,Z)-**16** and (Z,Z,Z)-**16**. Comparison of the spectral properties (UV, ^1H NMR and mass spectra) of the individual allofarnesenes isolated by preparative GLC with those of the third component of the fire ant trail pheromone demonstrated that the latter is the stereoisomer (Z,Z,Z)-**16**. Bioassays of the allofarnesene isomers demonstrated that the compounds (E,Z,E)-, (Z,Z,E)- and (E,Z,Z)-**16** with the (Z)-configuration of the C(4)=C(5) bond exhibit the trail pheromone activity.

The fourth and fifth components of the trail pheromone of *S. invicta* were identified¹⁵ as (Z,E)- and (E,E)-homofarnesenes **19** by comparing the physicochemical characteristics of these pheromone components with those of the compounds (Z,E)-, (E,E)-, (E,Z)- and (Z,Z)-**19**, which have been specially synthesised from nerol or geraniol.

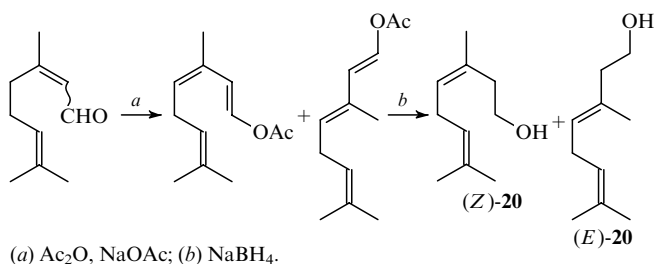


(a) PBr_3 , Py; (b) $\text{MeCH}(\text{SPh})_2$; (c) HgCl_2 ; (d) $\text{H}_2\text{C}=\text{C}(\text{Me})\text{MgBr}$; (e) PCC, CH_2Cl_2 ; (f) $\text{Ph}_3\text{P}=\text{CH}_2$.

2. Trail pheromone of the ant *Leptogenys diminuta*

In 1991, Attygalle *et al.*¹⁶ isolated the trail pheromone of the ants *Leptogenys diminuta*. Based on the results of physicochemical studies, the authors assigned the structure of (Z)-isogeraniol (**20**) to this pheromone. To decide between the (Z)- and (E)-configurations of compound **20**, the retention times (GLC) of the

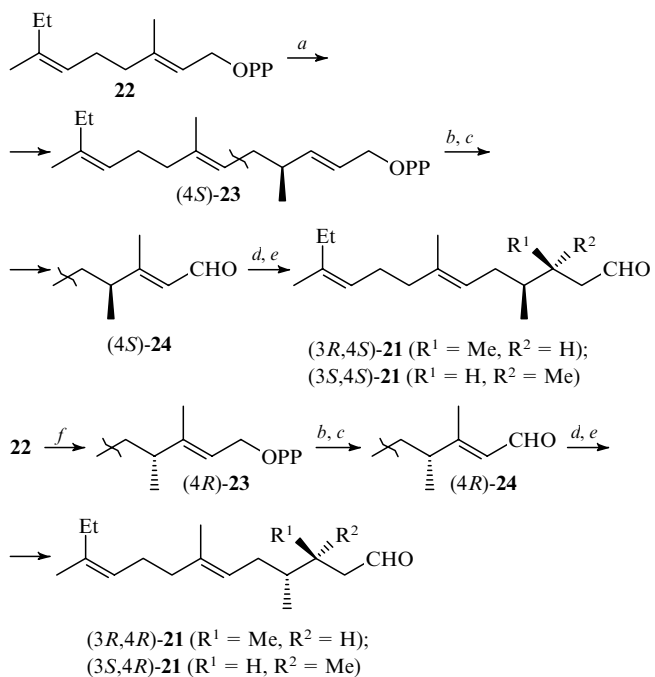
natural pheromone and the samples of (Z)- and (E)-**20** synthesised from citral enol acetates were compared.



3. Trail pheromone of Pharaoh's ant *Monomorium pharaonis* (faranal)

In 1977, Ritter *et al.*¹⁷ isolated the trail pheromone of Pharaoh's ant *Monomorium pharaonis*, which is a pest of food and a dangerous carrier of wound infections. Based on the results of physicochemical studies, the structure of 3,4,7,11-tetramethyldeca-(6E,10Z)-dienal was assigned to this pheromone named faranal. However, the absolute configurations of the C(3) and C(4) centres in the molecule remained an open question up to 1980 when Kobayashi and coworkers¹⁸ synthesised isomeric aldehydes **21** and demonstrated that only the compound (3S,4R)-**21** exhibited biological activity and, hence, the natural faranal had this configuration.

The key step of the synthesis involved condensation of (2E,6Z)-homogeraniol pyrophosphate **22** with (3E)- or (3Z)-3-methylpent-3-enyl pyrophosphate catalysed by farnesyl-pyrophosphate synthetase leading to chiral pyrophosphates (4S)- and (4R)-**23**, which was in accord with the results obtained previously.^{19,20} These compounds were converted into aldehydes (4S)- and (4R)-**24**, respectively. Selective reduction of the C(2)=C(3) double bond in the aldehydes (4S)-**24** and (4R)-**24** afforded a mixture of the diastereomeric aldehydes (3R,4S)- and (3S,4S)-**21**

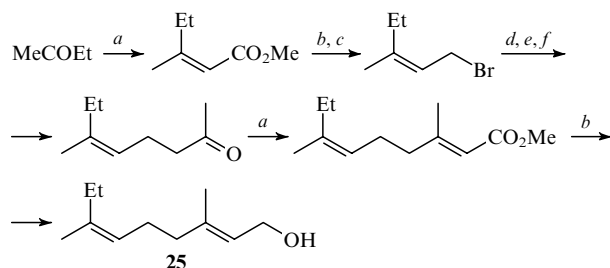


PP is $\text{P}_2\text{O}_6\text{H}_3$; (a) $\text{farnesyl-pyrophosphate synthetase}$; (b) alkaline phosphatase; (c) MnO_2 ; (d) Et_3SiH , $(\text{Ph}_3\text{P})_3\text{RhCl}$; (e) H_3O^+ ;

(f) $\text{farnesyl-pyrophosphate synthetase}$

and a mixture of the diastereomers (3*R*,4*R*)- and (3*S*,4*R*)-**21**, respectively. The individual compounds were isolated by HPLC.

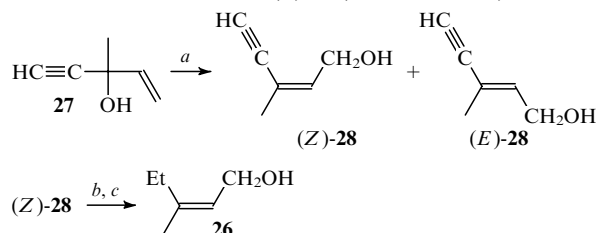
Homogeraniol **25** required for the preparation of the pyrophosphate **22** was synthesised²¹ using a reaction sequence in which the key step of chain elongation (*a*) was non-stereoselective and, hence, it was necessary to separate isomers by rectification or chromatography.



(*a*) (EtO)₂P(O)CH₂CO₂Me, MeONa; (*b*) LiAlH₄; (*c*) PBr₃, Py; (*d*) Mg, MeCOCH₂CO₂Me; (*e*) NaOH; (*f*) H₃O⁺.

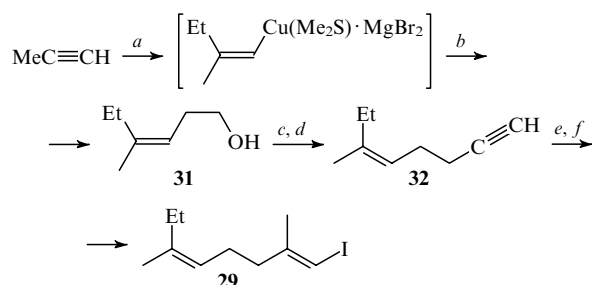
Generally, the synthesis of faranal [(3*S*,4*R*)-**21**] involves coupling of two building blocks. One of these blocks contains either only (*Z*)-trisubstituted alkene fragments or simultaneously (*Z*)- and (*E*)-trisubstituted fragments, while the second block contains the chiral portion of the molecule. The construction of the blocks of both types and their coupling to form the target faranal molecule [(3*S*,4*R*)-**21**] are considered below.

Mori and Ueda^{22, 23} used an allylic alcohol **26** as the (*Z*)-trisubstituted alkene synthon. Its synthesis involved isomerisation of 3-methylpent-1-en-4-yn-3-ol (**27**) under the action of lithium acetylide and reduction of the triple bond in the alcohol (*Z*)-**28** isolated from its mixture with (*E*)-**28** (the ratio 85 : 15).



(*a*) HC≡CLi, (*b*) NH₂NH₂·H₂O; (*c*) H₂O₂, EtOH.

Baker *et al.*²⁴ performed a highly stereoselective synthesis of the alkene synthon **29** based on the *cis*-addition of organocopper compounds to terminal alkynes (this reaction had been discovered by Corey and Katzenellenbogen²⁵). The reagent **30** was added to the starting propyne to give (*Z*)-homoallylic alcohol **31**. The alcohol **31** was converted into enyne **32** via tosylate. Successive treatment of compound **32** with a cuprate complex **33**²⁶ and iodine gave the target iodide **29** in 33.7% overall yield with a stereoselectivity exceeding 96%.

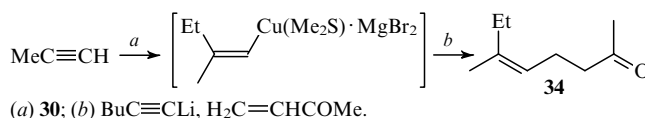


(*a*) EtCu(Me₂S)·MgBr₂ (**30**); (*b*) PrC≡CLi, , (*c*) TsCl, Py; (*d*) HC≡CLi; (*e*) MeCu(Me₂S)·MgBr₂ (**33**); (*f*) I₂.

An analogous scheme was used in the synthesis of faranal performed by Mori and coworkers.²⁷ They succeeded in increas-

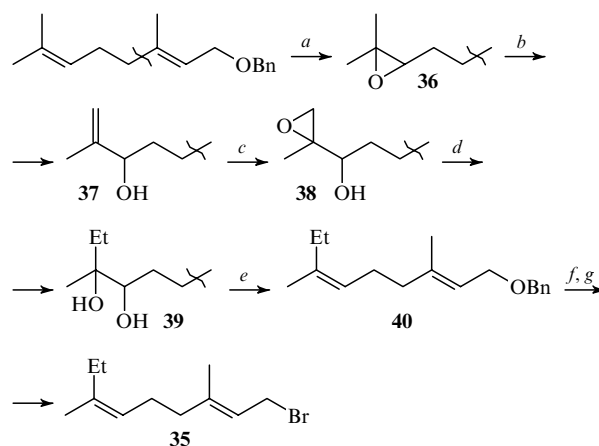
ing substantially the yield in the step of conversion of the enyne **32** into the iodide **29** by applying Wipf's modification²⁸ of carbocationic aluminination.

The synthon **34** was prepared employing the cuprate procedure for the construction of the (*Z*)-alkene fragment of faranal.²⁹



(*a*) **30**; (*b*) BuC≡CLi, H₂C=CHCOMe.

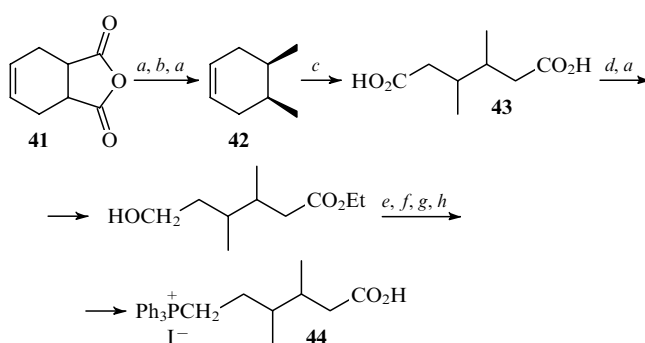
An alternative procedure for the construction of the (*Z*)-trisubstituted alkene fragment was used in the synthesis of bromide **35**, which is a key intermediate in the synthesis of faranal.^{30, 31} Epoxide **36**, which can readily be prepared from benzyl ether of geraniol, was converted into allylic alcohol **37** in high yield. Sharpless's epoxidation of the latter, scission of the epoxy group in the resulting epoxide **38** with lithium dimethyl cuprate and, finally, elimination of the hydroxy groups from diol **39** according to a procedure proposed by Tanaka *et al.*³² afforded benzyl ether **40**. The latter was converted into the bromide **35** according to standard procedures in a yield of 24% with respect to geraniol.



(*a*) *m*-Chloroperbenzoic acid (MCPBA); (*b*) (PrⁱO)₃Al, PhMe; (*c*) BuⁱO₂H, VO(acac)₂; (*d*) Me₂CuLi; (*e*) HC(OMe)₂NMe₂, Ac₂O; (*f*) Li/NH₃; (*g*) PBr₃, Py.

Conversions of the above-described alkene synthon blocks **26**, **29**, **34** and **35** into faranal [(3*S*,4*R*)-**21**] involved their coupling with blocks containing the 3,4-dimethylbutanal fragment. In many cases, an adduct of butadiene with maleic anhydride **41**, which was smoothly converted into *cis*-dimethylcyclohexene (**42**), was used as the starting compound for the preparation of these blocks. The ring-opening in the compound **42** and the transformation of dicarboxylic acid **43** giving rise to the target synthons have been performed in two ways. The path *I*²⁹ involved

Path *I*

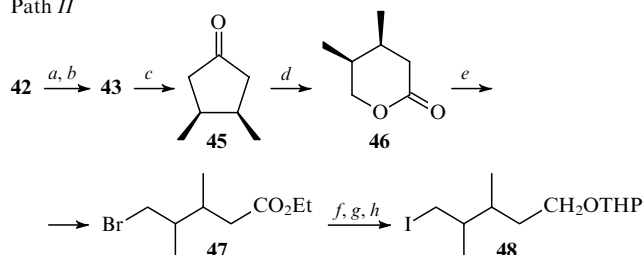


(*a*) LiAlH₄; (*b*) MeSO₂Cl, Py; (*c*) KMnO₄, Bu₄NHSO₄, H₂O-PhH; (*d*) EtOH, H₂SO₄, H₂O; (*e*) TsCl, Py; (*f*) LiI, MeCN; (*g*) NaOH; (*h*) Ph₃P, PhH.

oxidation of dimethylcyclohexene **42** with potassium permanganate under conditions of phase transfer catalysis followed by the transformation of the carboxy groups in the dicarboxylic acid **43** to form phosphonium salt **44**.

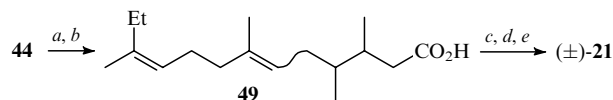
The path *II*²⁴ involved ozonation of dimethylcyclohexene **42** to form the acid **43**. Its pyrolysis afforded ketone **45** whose Baeyer–Villiger oxidation gave rise to lactone **46** (the total yield was 42.8% with respect to the adduct **41**). Treatment of the lactone **46** with anhydrous HBr in EtOH afforded bromo ester **47**, which was converted into iodide **48** according to standard procedures. The iodide **48** is a synthon for the construction of (±)-faranal.[†]

Path *II*



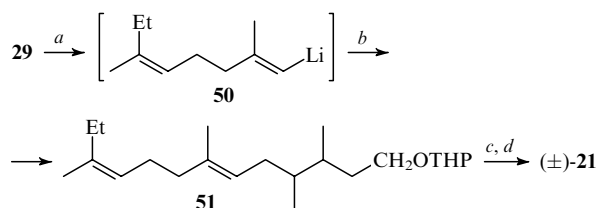
THP is tetrahydropyran-2-yl; (a) O₃; (b) CrO₃; (c) Ba(OH)₂, Δ; (d) MCPBA; (e) HBr, EtOH; (f) LiAlH₄; (g) 3,4-dihydro-2H-pyran (DHP), TsOH; (h) LiI, MeCN.

The target racemic faranal [(±)-**21**] was synthesised²⁹ by condensation of the ylide generated from the phosphonium salt **44** with the ketone **34**. The resulting 54:46 mixture of isomeric acids (6*E*)- and (6*Z*)-**49** was converted into a mixture of the racemic faranal [(±)-**21**] and its (6*Z*)-isomer through the corresponding ethyl esters and alcohols. The isomer (±)-**21** was isolated from the latter mixture by preparative GLC in 9.1% total yield.



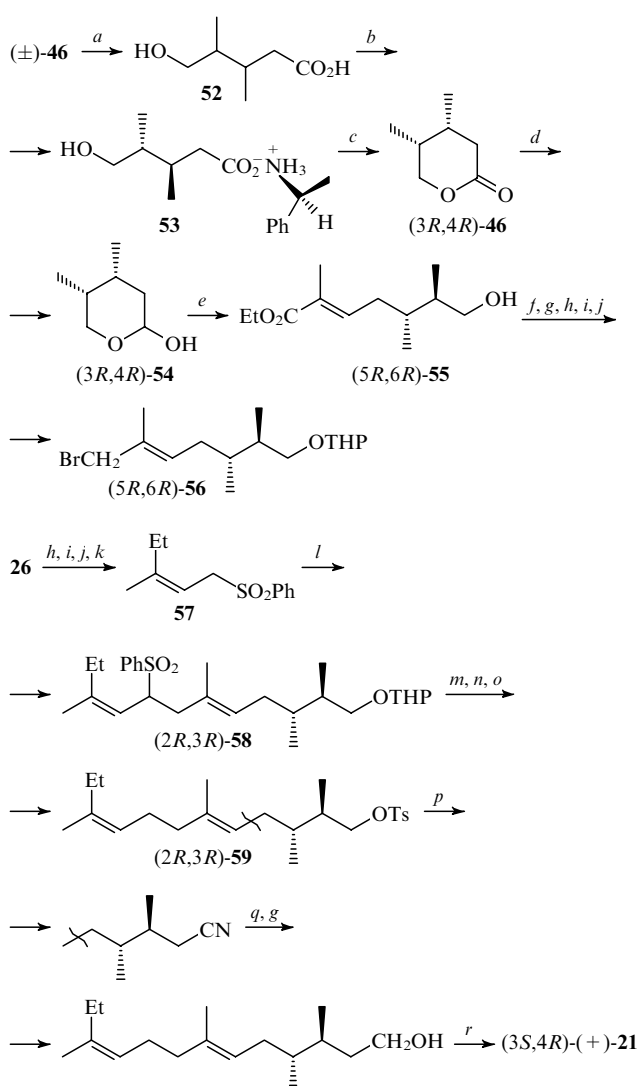
(a) NaH, DMSO; (b) **34**; (c) CH₂N₂; (d) LiAlH₄; (e) PCC, CH₂Cl₂.

To reach the same goal, Baker *et al.*²⁴ used condensation of a lithium derivative **50**, which was prepared from the iodide **29**, with the iodide **48**. This condensation is highly stereoselective. The resulting tetrahydropyranyl ether **51** was converted into the (±)-faranal [(±)-**21**] in a total yield of 18% with respect to the iodide **48**.



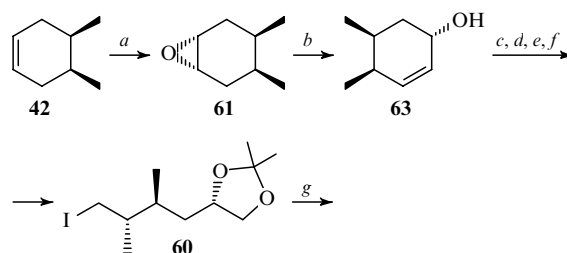
(a) Bu^tLi, Et₂O, −90 °C; (b) **48**, Et₂O–THF (1 : 3); (c) H₃O⁺; (d) PCC, CH₂Cl₂.

Mori and Ueda^{22,23} were the first to synthesise natural (3*S*,4*R*)-(+)-**21**. The key step of this scheme involved asymmetric resolution of hydroxy acid (±)-**52**, which was prepared from the lactone (±)-**46**, using treatment with (*S*)-(-)-α-phenylethylamine. Acidification of the resulting salt **53** afforded the lactone (+)-**46** whose (3*R*,4*R*)-configuration was confirmed by conversion into (*R*)-citronellic acid.

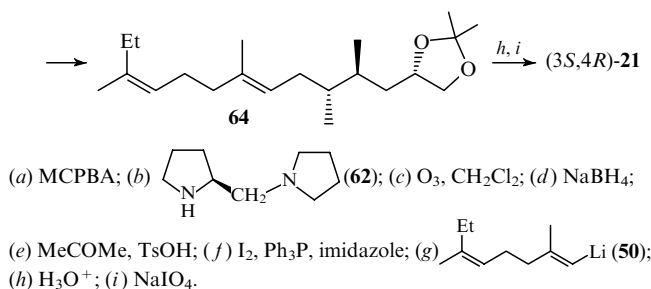


(a) NaOH; (b) (*S*)-(-)-α-phenylethylamine; (c) HCl; (d) Bu₂AlH; (e) (EtO)₂P(O)CH(Me)CO₂Et, NaOEt; (f) DHP, TsOH; (g) LiAlH₄; (h) BuLi; (i) TsCl; (j) LiBr, Et₂O–HMPA (hexamethylphosphoric triamide); (k) PhSO₂Na, DMF; (l) BuLi, THF–HMPA, (5*R*,6*R*)-**56**; (m) Li/NH₃; (n) H₃O⁺; (o) TsCl, Py; (p) NaCN, DMSO; (q) NaOH, EtOH; (r) PCC, CH₂Cl₂.

Reduction of (3*R*,4*R*)-**46** into chiral lactol **54** followed by the Horner–Emmons reaction of the latter with triethyl 2-methyl-2-phosphonoacetate afforded hydroxy ester (5*R*,6*R*)-**55**, which was converted into bromide (5*R*,6*R*)-**56** using a sequence of standard reactions. The chiral bromide (5*R*,6*R*)-**56** was condensed with sulfone **57** prepared from the alcohol **26**. Desulfation of the resulting sulfone **58** followed by the replacement of the protective group afforded tosylate (2*R*,3*R*)-**59**, which was the starting product in the final steps of the synthesis of faranal [(3*S*,4*R*)-(+)-**21**] identical with the natural specimen.



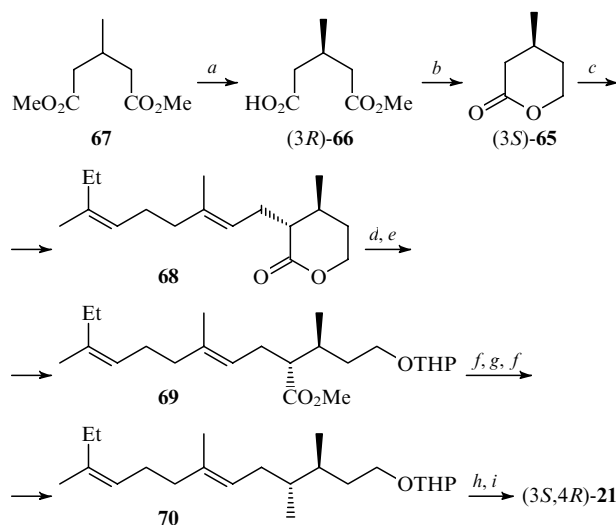
[†] Recently, Tolstikov and coworkers³³ have reported an efficient synthesis of methoxymethyl analogues of the compound **48**.



Later, Mori and Murata²⁷ developed a shorter synthetic route to faranal [(3*S*,4*R*)-(+)-21]. The key chiral synthon for this compound, *viz.*, iodide **60**, was prepared in five steps starting from dimethylcyclohexene **42**. The asymmetric resolution of *meso*-epoxide **61** using the lithium derivative of (*S*)-pyrrolidin-2-ylmethylpyrrolidine (**62**) afforded allylic alcohol **63**, which was purified by recrystallisation of the corresponding 3,5-dinitrobenzoate to *ee* ~ 100%. Ozonation of the compound **63**, reduction and protection of the hydroxy groups at C(1) and C(2) in the resulting triol followed by substitution of the hydroxy group at C(6) gave rise to the iodide **60**. Condensation of **60** with 6-ethyl-2-methylhepta-1,5-dienyllithium (**50**) resulted in enantiomerically pure acetal **64**. Hydrolysis of **64** followed by periodate oxidation of the resulting diol gave rise to (3*S*,4*R*)-21 (in a total yield of 12.5% with respect to propyne), which was used for the preparation of the lithium derivative **50**.

The chiral fragment of faranal was constructed also with the use of lactone (3*S*)-**65** formed from methyl hydrogen (3*R*)-3-methylglutarate [(3*R*)-**66**].^{30,31} Enzymic hydrolysis of the dimethyl ester **67** using pig liver esterase (PLE) afforded the ester **66** with an optical purity of 85%. This ester was purified by recrystallisation of 1-cinchonidinium salt to *ee* 100%.

Alkylation of the enolate prepared from lactone **65** with the bromide **35** gave rise to lactone (2*R*,3*S*)-**68** containing ~ 6% of the (2*S*,3*S*)-isomer. Transesterification of the lactone **68** followed by protection of the hydroxy group in the resulting hydroxy ester afforded ester **69** whose methoxycarbonyl group was converted into the methyl group in three standard steps. The resulting tetrahydropyranyl ether **70** was converted into (3*S*,4*R*)-21 in a total yield of ~ 2% with respect to geraniol, which was the starting compound for the preparation of the bromide **35**.

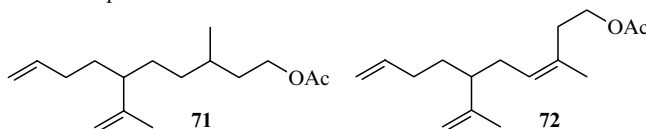


IV. Syntheses of insect sex pheromones

1. Synthesis of sex pheromones of scales

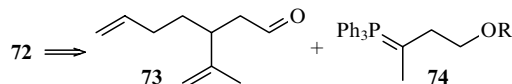
a. Sex pheromone of the California red scale

Roelofs *et al.*^{34,35} isolated the female-produced sex pheromone of the California red scale *Aonidiella auranti*, which is the major pest of citrus crops distributed throughout the tropical and subtropical regions. This pheromone was found to consist of two components. Based on the data of physicochemical studies, it was proposed that these components have structures **71** and **72**.

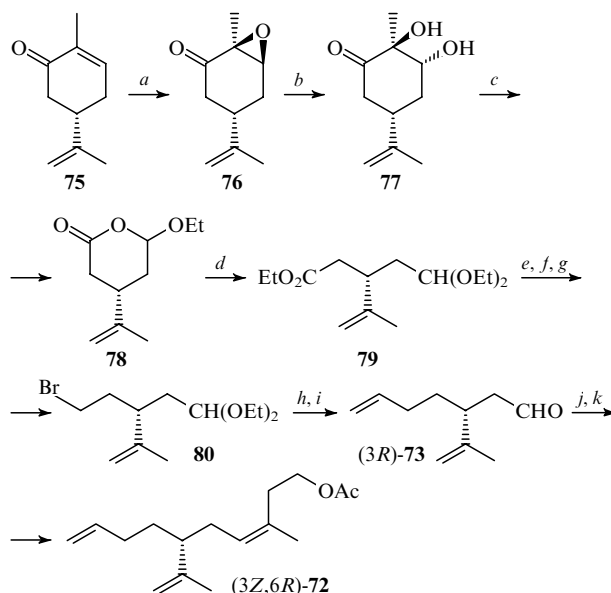


Due to the deficiency of the isolated natural substance, the absolute configurations of these compounds were established only by comparing the physicochemical characteristics of the pheromone components with those of all possible isomers synthesised starting from (*S*)- and (*R*)-carvone. It was found that only the (3*S*,6*R*)-acetate **71** and the (3*Z*,6*R*)-acetate **72** exhibit the pheromone activity.

The retrosynthetic analysis of the molecule **72** shows that the simplest approach to its construction involves the Wittig reaction between synthon blocks **73** and **74**. This approach was used in the first synthesis of the compound **72**.³⁶



The aldehyde (3*R*)-**73** was prepared by oxidative scission of (*S*)-carvone (**75**) *via* epoxide **76** and diol **77**. Ethoxy lactone **78** prepared from the diol **77** was converted into compound **79** and then into bromide **80** in three standard steps. Treatment of the bromide **80** with vinyl lithium followed by hydrolysis afforded the aldehyde **73**.

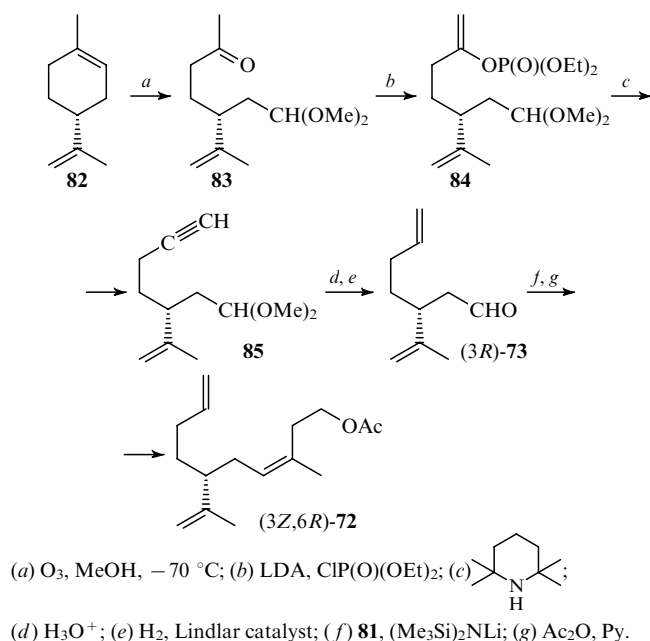


(a) H₂O₂, NaOH; (b) HClO₄, H₂O, THF; (c) Pb(OAc)₄, EtOH; (d) HC(OEt)₃, TsOH, EtOH; (e) LiAlH₄; (f) TsCl, Py; (g) NaBr, HMPA; (h) CH₂=CHLi; (i) H₃O⁺; (j) Ph₃P⁺CH(Me)(CH₂)₂OH Br[−] (**81**), 2 equiv. of BuLi; (k) Ac₂O, Py.

The reaction of the aldehyde **73** with ylide obtained from phosphonium salt **81** gave rise to a 52:48 mixture of isomeric alcohols. Separation of a mixture of (3*Z*)- and (3*E*)-acetates **72**

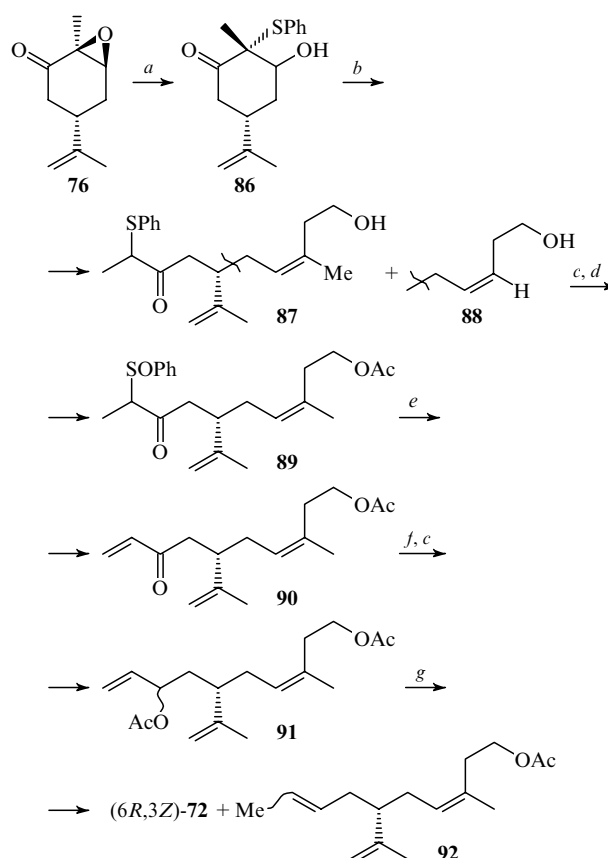
obtained from these alcohols by preparative GLC afforded compound (3Z,6R)-**72** in 2.53% total yield.[‡]

The acetate (3Z,6R)-**72** was also synthesised³⁷ starting from (R)-limonene **82** according to a similar strategy, but using a more efficient procedure. Ozonolysis of limonene **82** yielded oxo acetal **83**, which was converted into enyne acetal **85** through hydroxy acetal phosphate **84** according to Negishi.³⁸ Hydrolysis of the latter yielded aldehyde, which was subjected to hydrogenation to form the diene aldehyde (3R)-**73**. Condensation of the latter with ylide generated by the reaction of (Me₃Si)₂NLi with the phosphonium salt **81** afforded a 2:1 mixture of isomeric alcohols, which were separated by chromatography. Acetylation of the (3Z)-isomer produced (3Z,6R)-**72** in 37% total yield.



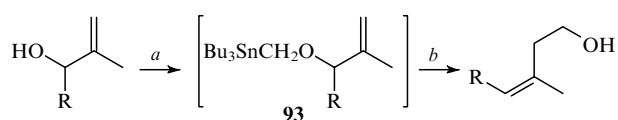
A substantial drawback of the above-considered syntheses of the acetate **72** is the non-stereoselectivity of the key step of the construction of the (Z)-trisubstituted C=C bond by the Wittig reaction. Caine and Crews³⁹ have overcome this drawback using another synthetic scheme. It appeared that when treated with the ylide, which was generated from the salt **81** under the action of BuLi in a mixture of THF and HMPA, β-hydroxy α-phenylthio ketone **86** prepared from the oxirane **76**⁴⁰ underwent the retro-aldol reaction followed by the Wittig olefination to form alcohol (3Z)-**87**. This compound did not contain an admixture of the (3E)-isomer but was contaminated with desmethyl analogue **88** (~15%). The resulting mixture was converted into a mixture of the corresponding acetoxy sulfoxides from which sulfoxide **89** was isolated by chromatography. Thermal desulfinylation of the sulfoxide **89** afforded trienone **90**, which was converted into a mixture of diacetates **91**. Hydrogenolysis of the acetates **91** yielded a 89:11 mixture of the pheromone (3Z,6R)-**72** and its regioisomer **92**. Separation of this mixture was a very tedious procedure. Thus, in spite of the stereoselectivity of the construction of the (Z)-trisubstituted C=C bond, this scheme has no advantages over the scheme proposed by Becker and Sahali³⁷ as regards both the number of steps and the yield of the target compound **72**.

Still and Mitra⁴¹ developed a more efficient procedure for the stereoselective construction of the (Z)-trisubstituted alkene fragment in the compound **72**. It was found that the reactions of BuLi with allylic trialkylstannylmethyl ethers of the type **93** were



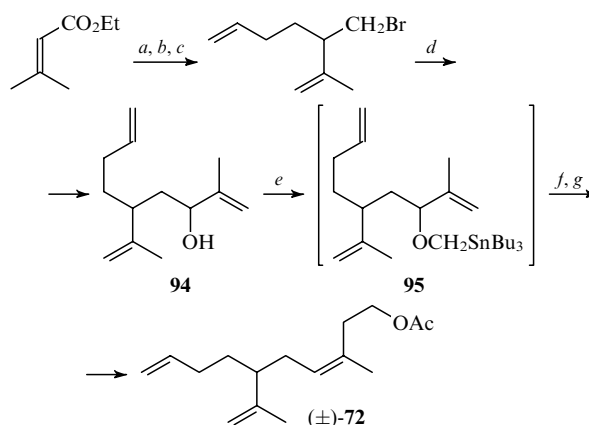
(a) PhSH, Et₃N, MeCN; (b) **81**, 2 equiv. of BuLi, THF, HMPA; (c) Ac₂O, Py; (d) MCPBA; (e) 135 °C, 0.15 mm Hg; (f) LiAlH₄; (g) HCO₂NH₄, PdCl₂(PPh₃)₂, dioxane.

accompanied by a [2,3]-sigmatropic rearrangement yielding (Z)-trisubstituted homoallyl alcohols.



R = Alk; (a) KH, Bu₃SnCH₂I; (b) BuLi.

This finding has been used in the synthesis of the racemic acetate **72**. The key intermediate, viz., alcohol **94**, was prepared in four steps starting from ethyl 3-methylcrotonate. The transforma-

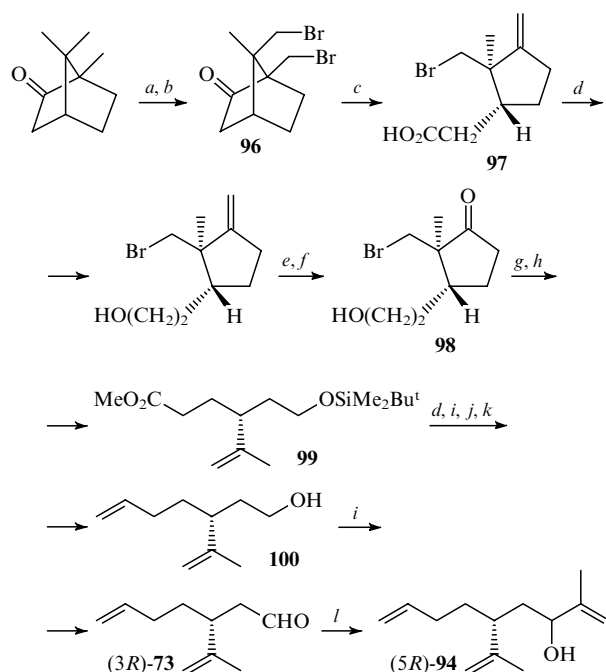


(a) LDA, CH₂=CH(CH₂)₂Br; (b) LiAlH₄; (c) N-bromosuccinimide (NBS), PPh₃; (d) Mg, H₂C=C(Me)CHO; (e) KH, Bu₃SnCH₂I; (f) BuLi; (g) Ac₂O, Py.

[‡] Simultaneously, the isomer (3E,6R)-**72** was isolated; the isomers (3Z,6S)-**72** and (3E,6S)-**72** were prepared analogously starting from (R)-carvone.

tion of the skeleton of the alcohol **94** through organotin compound **95** followed by acetylation afforded ($\pm$)-**72** in 32% total yield with the stereoselectivity exceeding 95%.

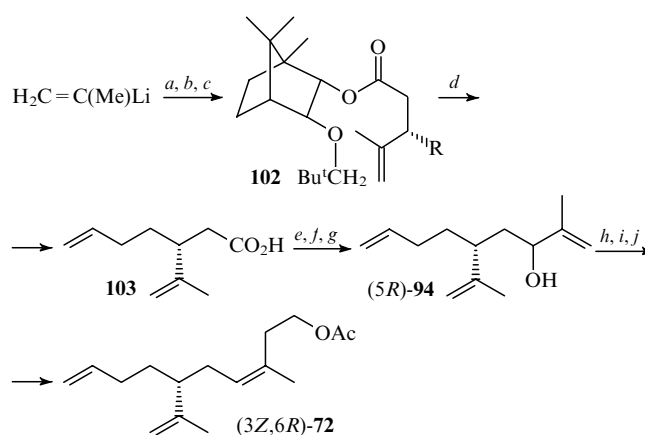
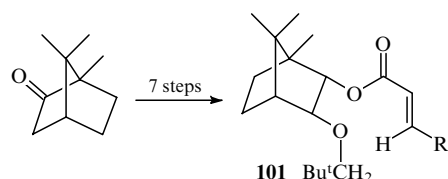
The acetate (3*Z*,6*R*)-**72** was also synthesised^{42,43} using the Still rearrangement. The required alcohol (5*R*)-**94** was prepared⁴² from (+)-camphor. An efficient enantiospecific procedure developed previously^{44–46} for the cleavage of 9,10-dibromocamphor **96** yielding bromoacid **97** has been employed.



(a) Br₂, ClSO₃H; (b) Zn, AcOH; (c) KOH, DMSO, H₂O; (d) LiAlH₄; (e) O₃, MeOH; (f) Me₂S; (g) Bu^tMe₂SiCl, 4-Me₂NC₃H₄N; (h) NaOMe, MeOH; (i) PDC, CH₂Cl₂; (j) H₂C=PPh₃; (k) Bu₄NF; (l) H₂C=C(Me)MgBr.

Substituted cyclopentanone **98**, which was synthesised from compound **97** according to standard procedures, is (like compound **96**) a β -bromo ketone and underwent smooth ring-opening following protection of the hydroxy group to form acyclic ester **99**. The latter was transformed into dienol **100** and then into the aldehyde (3*R*)-**73** according to standard procedures. The reaction of the aldehyde (3*R*)-**73** with isopropenylmagnesium bromide afforded the alcohol (5*R*)-**94** in 8% total yield. Since the conversion of the alcohol ($\pm$)-**94** to the acetate ($\pm$)-**72** had been already performed by Still and Mitra,⁴¹ the above-described procedure for the preparation of (5*R*)-**94** can be formally considered as the first total stereoselective synthesis of (3*Z*,6*R*)-**72**.

Oppolzer and Stevenson⁴³ synthesised the acetate (3*Z*,6*R*)-**72** also with the use of (+)-camphor, but this was used as a chiral matrix rather than as a synthon. This approach was based on the known fact⁴⁷ that alkenyl cuprates stabilised by Bu₃P add with high stereoselectivity to enoates of the type **101** prepared from camphor. In this case, the induced chirality is completely retained after removal of the matrix.

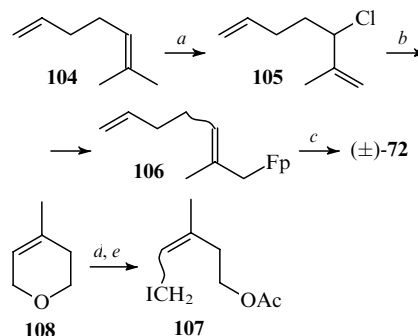


R = (CH₂)₂CH=CH₂; (a) Bu₃P, CuI, -70 °C; (b) BF₃·Et₂O; (c) **101**; (d) NaOH, EtOH, H₂O; (e) LiAlH₄; (f) (COCl)₂, DMSO, Et₃N; (g) H₂C=C(Me)Li; (h) KH, Bu₃SnCH₂I; (i) BuLi; (j) Ac₂O, Py.

Thus enoate **101** [prepared from (+)-camphor in seven steps] added the complex of diisopropenyl cuprate with Bu₃P to form ester **102** with an enantioselectivity of ~95%. Saponification of the ester **102** afforded chiral acid **103**. This acid was converted into the alcohol (5*R*)-**94** according to standard procedures. The latter was transformed into (3*Z*,6*R*)-**72** using the Still rearrangement in 20% total yield.

The synthesis of the triene **72** still attracts interest. This pheromone serves as a test substance for examining every new method proposed for the construction of (*Z*)-trisubstituted C=C bonds.

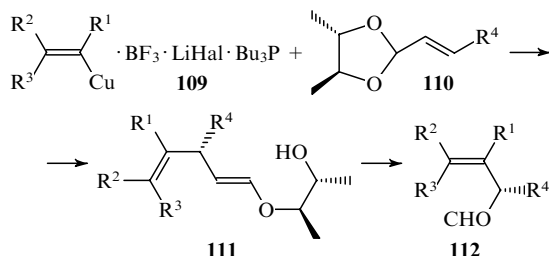
Thus the compound **72** was chosen⁴⁸ as one of the subjects for the comparison of the reactivities of allylic organoiron nucleophiles with those of allylsilanes and allylstannanes. The synthesis of ($\pm$)-**72** involved the conversion of the commercially available diene **104** into a mixture (~1 : 1) of organoiron compounds (2*Z*)- and (2*E*)-**106** via allylic chloride **105**. The second synthon required for the construction of the triene **72**, viz., iodide **107** (a ~1 : 1 mixture of the isomers), was prepared from 4-methyl-5,6-dihydro-2*H*-pyran **108** according to standard procedures.



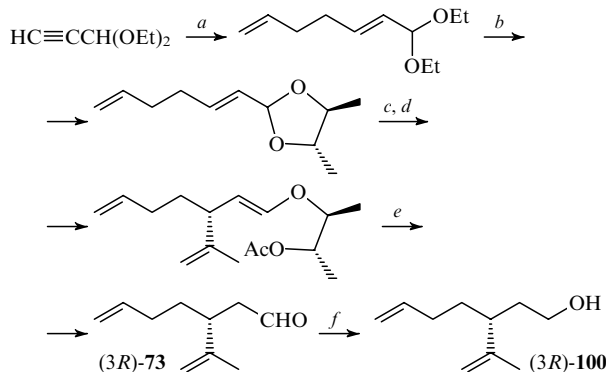
Fp = C₅H₅Fe(CO)₂; (a) Ca(OCl)₂; (b) NaFp; (c) **107**, MeNO₂; (d) AcCl, K[PtCl₃(C₂H₄)]; (e) NaI, Me₂CO.

In spite of the geometric inhomogeneity of the iodide **107**, its condensation with organoiron derivatives **106** at ~20 °C afforded ($\pm$)-**72** (the yield was 42%) containing <1% of an admixture of the (3*E*)-isomer. The selectivity of the reaction was attributed to the high reactivity of the (3*Z*)-iodide **107** due to the anchimeric assistance to ionisation provided by the acetoxy group. This scheme is attractive because it involves a small number of steps and does not require the introduction and removal of protective groups.

The syntheses of the aldehyde (3*R*)-**73** and the alcohol (3*R*)-**100**,⁴⁹ which are the key intermediates in the synthesis of (3*Z*,6*R*)-**72**, were carried out with the use of a previously discovered 1,4-addition of complex organocopper compounds of the type **109** to acetals **110** prepared from α,β -enals and (*R,R*)-butane-2,3-diol. Dienol ethers **111** prepared by the highly regio- and diastereoselective reaction were subjected to hydrolysis to form aldehydes **112** in quantitative yields.



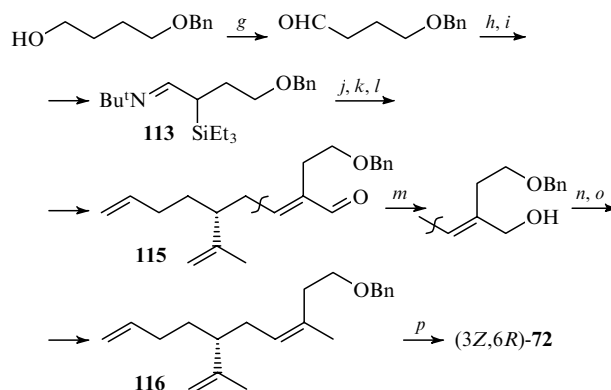
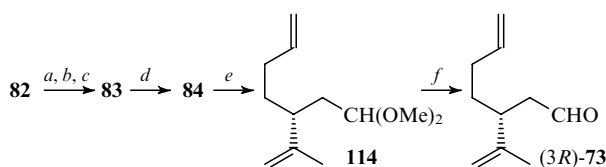
This scheme was tried out in the synthesis of the aldehyde (3*R*)-**73** starting from propargylaldehyde diethyl acetal (the yield was 50%, *ee* 85%). The aldehyde (3*R*)-**73** was reduced to the alcohol (3*R*)-**100** in quantitative yield.



(a) [H₂C=CH(CH₂)₂]₂CuLi; (b) (2*R*,3*R*)-HOCH(Me)CH(Me)OH, TsOH; (c) H₂C=C(Me)Cu·LiBr·BF₃·PBu₃; (d) Ac₂O, Py; (e) HCO₂H; (f) NaBH₄.

The aldehyde (3*Z*,6*R*)-**72** was also synthesised⁵⁰ using a highly stereoselective procedure developed by one of the authors^{51–53} of the present review for the construction of (*Z*)-tri-substituted alkenes based on the facts that (*E*)-isomers of α,β -disubstituted acroleins are thermodynamically favourable and that they are stereospecifically converted into (*Z*)-trisubstituted alkenes.

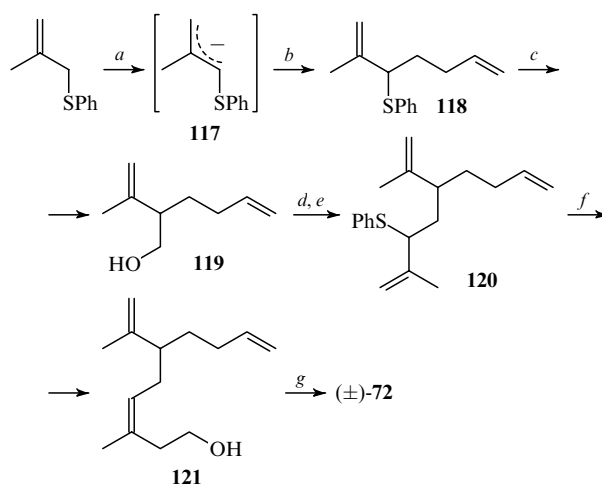
According to this methodology, Baudouy and Prince⁵⁰ chose the aldehyde (3*R*)-**73** and α -(triethylsilyl)imine **113** as synthons for the construction of (3*Z*,6*R*)-**72**. The aldehyde (3*R*)-**73** was prepared from limonene according to a scheme reported previously.³⁷ However, Baudouy and Prince⁵⁰ developed a direct procedure for the conversion of the hydroxy acetal phosphate **84** into diene acetal **114**, which made it possible to reduce the scheme by two steps. The aldehyde (3*R*)-**73** was formed upon hydrolysis of the acetal **114** in quantitative yield. The second synthon, *viz.*, silylated imine **113**, was prepared in three standard steps starting from the monobenzy ether of butane-1,4-diol.



(a) O₃, MeOH; (b) (H₂N)₂CS; (c) HC(OMe)₃, CeCl₃·6 H₂O; (d) LDA, CIP(O)(OEt)₂, THF; (e) Li/NH₃, THF; (f) HClO₄, THF, H₂O; (g) (COCl)₂, DMSO, Et₃N; (h) Bu^tNH₂, 4 Å molecular sieves; (i) LDA, Et₃SiCl; (j) Bu^sLi, (3*R*)-**73**; (k) H₃O⁺; (l) C₅H₅N·HCl, CH₂Cl₂; (m) LiAlH₄, Et₂O; (n) C₅H₅N·SO₃, THF; (o) LiAlH₄, THF; (p) Ac₂O, HClO₄.

Condensation of the imine **113** deprotonated under the action of Bu^sLi with the aldehyde (3*R*)-**73** afforded acrolein **115**. The mixture formed initially was kept in a CH₂Cl₂ solution containing pyridinium chloride for 4 h after which the content of the (*Z*)-isomer was no higher than 1%. The carbonyl group in compound **115** was reduced to the methyl group in three standard steps. The replacement of the protective benzyl group in the resulting ether **116** by the acetate group gave rise to (3*Z*,6*R*)-**72** in 30% total yield.

The construction of the pheromone (±)-**72**⁵⁴ based on a method for the generation of allyllithium compounds by reductive lithiation of readily available allyl phenyl sulfides with aromatic radical anions^{55–57} has proved the utility of this procedure. The regiocontrolled addition of unsymmetrical allyllithium derivatives to carbonyl compounds (which had been developed by the authors previously) employed in this synthesis is of particular interest. Thus treatment of the allyllithium intermediate with Ti(OPr)₄ allows one to perform the subsequent reaction with an aldehyde at the more substituted position of the allylic system, whereas treatment with CeCl₃, on the contrary, makes it possible to perform this reaction at the less substituted position.

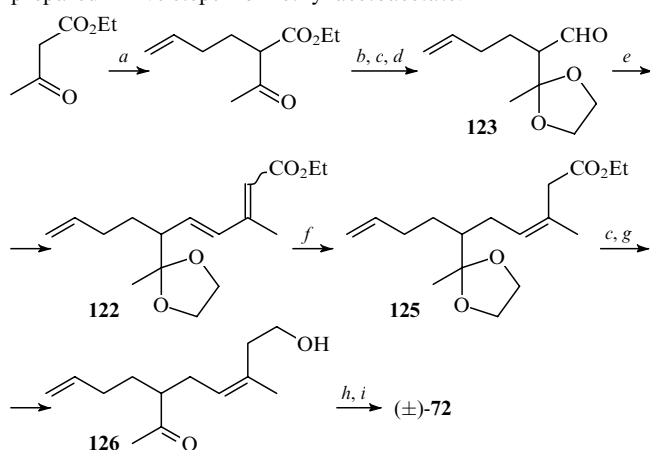


(a) Bu^sLi; (b) H₂C=CH(CH₂)₂Br; (c) lithium 4,4'-di(*tert*-butyl)bi-phenylide (LDBB), –78 °C, Ti(OPr)₄, CH₂O; (d) CBr₄, Ph₃P; (e) **117**; (f) LDBB, –78 °C, CeCl₃, CH₂O; (g) Ac₂O, Py.

Thus alkylation of the anion **117** generated from isobutenyl phenyl sulfide under the action of Bu^sLi with but-3-enyl bromide occurred exclusively at the α position to form sulfide **118**. Reductive lithiation of the latter with lithium 4,4'-di(*tert*-butyl)-

biphenylide followed by *in situ* treatment of the reaction product with $\text{Ti}(\text{OPr})_4$ and the reaction of the resulting organotitanium compound with formaldehyde afforded alcohol **119**, which was converted into allyl sulfide **120**. The sulfide **120** was subjected to reductive lithiation. The successive treatment of the resulting alkyllithium intermediate with CeCl_3 and formaldehyde gave rise to alcohol (3*Z*)-**121** from which the acetate ($\pm$)-**72** was obtained in 22.4% total yield.

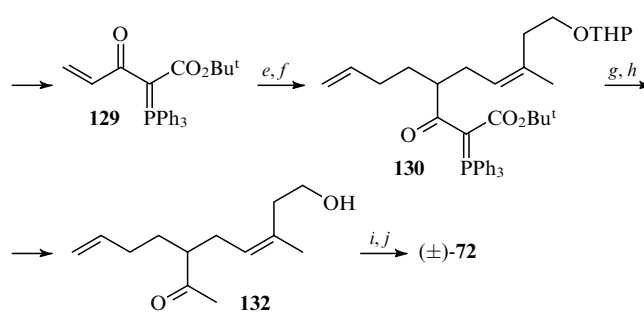
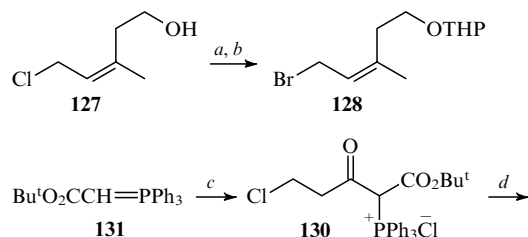
In 1995, Serebryakov and coworkers⁵⁸ synthesised the acetate ($\pm$)-**72** using the highly selective 1,4-*cis*-hydrogenation of conjugated dienes in the presence of carbonyl chromium complexes⁵⁹ for the construction of the (*Z*)-trisubstituted $\text{C}=\text{C}$ bond. This method had been employed previously^{60,61} in the synthesis of natural compounds. The triene **122** required for this synthesis was prepared in five steps from ethyl acetoacetate.



(a) EtONa , EtOH , $\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_2\text{Br}$; (b) $\text{HO}(\text{CH}_2)_2\text{OH}$, TsOH ; (c) LiAlH_4 ; (d) PCC , CH_2Cl_2 ; (e) $(\text{EtO})_2\text{P}(\text{O})\text{CH}_2\text{CH}(\text{Me})=\text{CHCO}_2\text{Et}$ (**124**), KOH , PhH , 18-crown-6 (18-C-6); (f) H_2 , $(\text{PhCO}_2\text{Me})\text{Cr}(\text{CO})_3$, Me_2CO , 120°C ; (g) H_3O^+ ; (h) $\text{Ph}_3\text{P}=\text{CH}_2$; (i) Ac_2O , Na_2CO_3 , 100°C .

Alkylation of ethyl acetoacetate with but-3-enyl bromide, the conversion of the resulting oxo ester (after protection of the carbonyl group) into hydroxy ketal and oxidation of the latter afforded aldehyde **123**. Condensation of **123** with triethyl 3-methyl-4-phosphonocrotonate (**124**) under conditions of phase transfer catalysis according to a procedure developed previously⁶² gave rise to a 2:1 mixture of the trienes (2*E*)- and (2*Z*)-**122**. Hydrogenation of the conjugated diene system in the presence of a chromium complex afforded (3*Z*)-ester **125**, which virtually did not contain an admixture of the (3*E*)-isomer. The ester **125** was converted into hydroxy ketone **126** by standard procedures. The reaction of the ketone **126** with methylidenetriphenylphosphorane followed by acetylation of the resulting alcohol completed the synthesis of ($\pm$)-**72** (the total yield was 4.3%).

In the synthesis of the compound **72**, Cooke and Burman⁶³ did not develop a new approach to the construction of the (*Z*)-trisubstituted $\text{C}=\text{C}$ bond but used the available (*Z*)-alkene fragment in chlorohydrin **127** (*Z* > 98%), which had been described previously⁶⁴ and which was converted into bromide **128** in two steps.

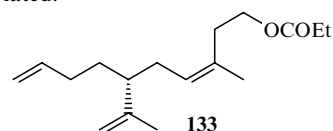


(a) DHP , HCl ; (b) NaBr , *N*-methylpyrrolidone; (c) $\text{Cl}(\text{CH}_2)_2\text{COCl}$; (d) MeONa ; (e) $\text{H}_2\text{C}=\text{CHCH}_2\text{Li}$; (f) **128**; (g) AcOH , 90°C ; (h) NaOH ; (i) Ac_2O , Py ; (j) $\text{Ph}_3\text{P}=\text{CH}_2$.

In the study cited (Ref. 63), an ingenious method for the assembly of the molecule ($\pm$)-**72** was used. Phosphorane **129** was used as the key compound in this synthetic scheme. The compound **129** was generated from phosphonium salt **130**, which was prepared by acylation of *tert*-butoxycarbonylmethylidenetriphenylphosphorane **131** with β -chloropropionyl chloride. Successive treatment of the phosphorane **129** with prop-2-enyllithium and the bromide **128** afforded the phosphorane **130** containing the major structural fragments of the pheromone ($\pm$)-**72**. The phosphorane **130** was converted into hydroxy ketone **132** by a procedure developed previously.⁶⁵ Acetylation of the latter followed by the reaction of the resulting acetate with methylidenetriphenylphosphorane gave rise to ($\pm$)-**72** in 8.5% total yield.

b. Sex pheromone of the white peach scale

Subsequent to the pheromone of the California red scale **72**, a structurally similar female-produced sex pheromone of the white peach scale *Pseudaulascaspis pentagona*, viz., propionate **133**, was isolated.⁶⁶

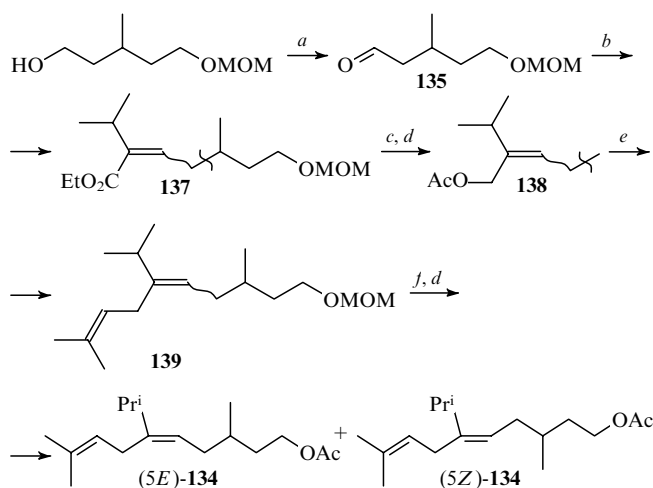


The structure of compound **133** was established by physicochemical methods and the absolute configuration of the C(6) centre was determined based on the results of bioassays of both enantiomers, which have been synthesised starting from (+)- and (−)-limonenes according to a scheme analogous to that used in the synthesis of the acetate **72** (see Section IV.1.a). Only the (3*Z*,6*R*)-propionate **133** appeared to be the active attractant.⁶⁷

Serebryakov and coworkers⁵⁸ performed a highly stereoselective synthesis of the compound **133** according to a procedure analogous to that developed by them for the pheromone **72**.

c. Sex pheromone of the yellow scale

Gieselmann *et al.*⁶⁸ isolated the female-produced sex pheromone of the yellow scale *Aonidiella citrina*, a species morphologically very similar to *A. auranti*, and established its structure. Although the pheromone of the yellow scale (3*R*,5*E*)-**134** is formally the (5*E*)-isomer, we consider this compound in the present review because the branches of its major hydrocarbon chain, like those in the pheromones of the California red scale and the white peach scale, are in the *cis* positions with respect to each other. Because of this, (3*R*,5*E*)-**134** was synthesised according to procedures analogous to those used for the preparation of pheromones containing the (*Z*)-trisubstituted $\text{C}=\text{C}$ bond. Based on the results of physicochemical studies,⁶⁸ the structure (5*E*)-**134** was assigned to this pheromone [with the accuracy of the absolute configuration of the C(3) centre]. This structure was confirmed by two independent syntheses. One of these syntheses⁶⁹ involved the Horner–Emmons reaction of aldehyde **135** with an anion generated from phosphonate **136**.



MOM is methoxymethyl; (a) PCC, AcONa, CH_2Cl_2 ; (b) $(\text{EtO})_2\text{P}(\text{O})\text{CH}(\text{Pr}^i)\text{CO}_2\text{Et}$ (**136**), EtONa; (c) Bu_2AlH ; (d) Ac_2O , Py; (e) $(\text{Me}_2\text{C}=\text{CH})_2\text{CuLi}$; (f) $\text{Cl}_3\text{CCO}_2\text{H}$.

The resulting mixture (4 : 1) of the esters (Z)- and (E)-**137** was converted into a mixture of acetates **138** through the corresponding alcohols. Treatment of the compounds **138** with diisobutyl-lithium cuprate afforded a mixture of isomers **139**, which was converted into a mixture of acetates (E)-**134** and (Z)-**134** in two standard steps also in a ratio of 1 : 4. Bioassays of the isomers separated by preparative GLC demonstrated that only the compound (E)-**134** exhibited the attractant activity.

Suguro *et al.*⁷⁰ reached the same conclusion when performing the stereoselective synthesis of the isomeric acetates **134** from the common precursor, *viz.*, ester (E)-**140**. This ester was prepared with a stereoselectivity of 92% by the *in situ* Claisen–Johnson [3,3]-sigmatropic rearrangement of orthoester **141** (Scheme 1).

Treatment of the ester **140** with MeMgI afforded alcohol **142**, which was dehydrated to form a mixture of regioisomeric trienes **143**. Hydroboration of this mixture under standard conditions gave rise to a mixture of the corresponding alcohols from which

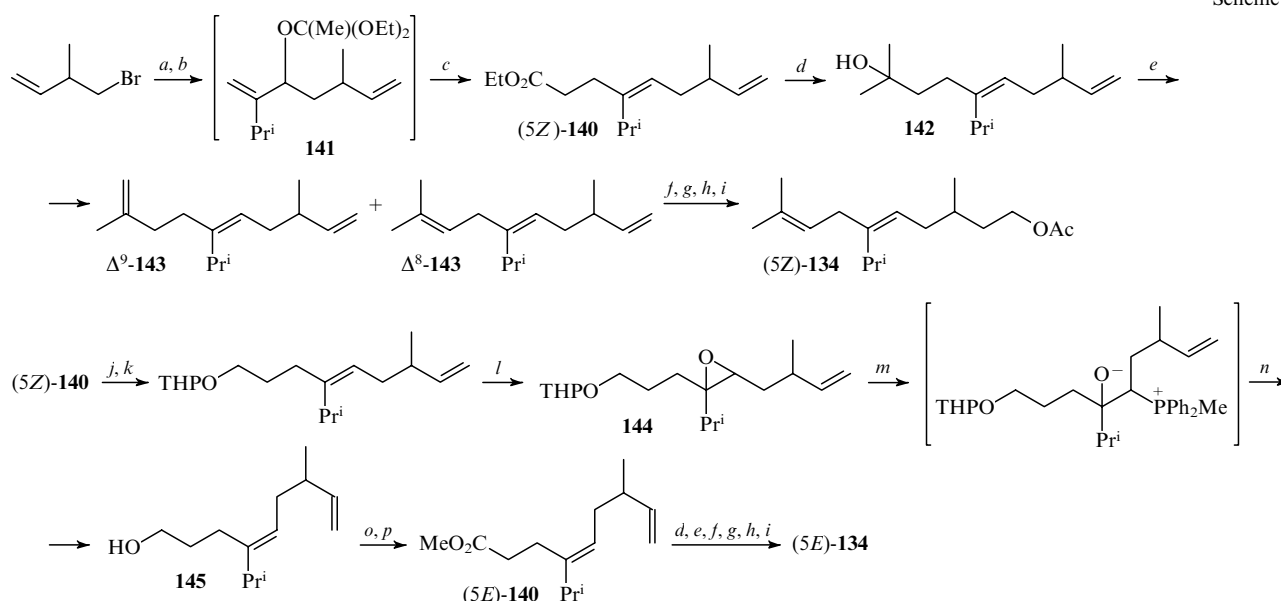
the (5Z)-isomer was isolated by chromatography. Acetylation of the latter afforded the acetate (5Z)-**134** in ~ 1% total yield.

The ester (E)-**140** required for the preparation of the acetate (E)-**134** was synthesised *via* epoxide **144** by the Vedejs method.⁷¹ Successive treatment of the epoxide **144** with lithium diphenylphosphide and methyl iodide afforded the corresponding tetrahydropyranyl derivative, which was converted into alcohol **145**. Oxidation of the hydroxy group in the alcohol **145** and methylation of the resulting carboxylic acid gave rise to the ester (E)-**140**, which was converted into (E)-**134** in 0.5% total yield by an analogous procedure.

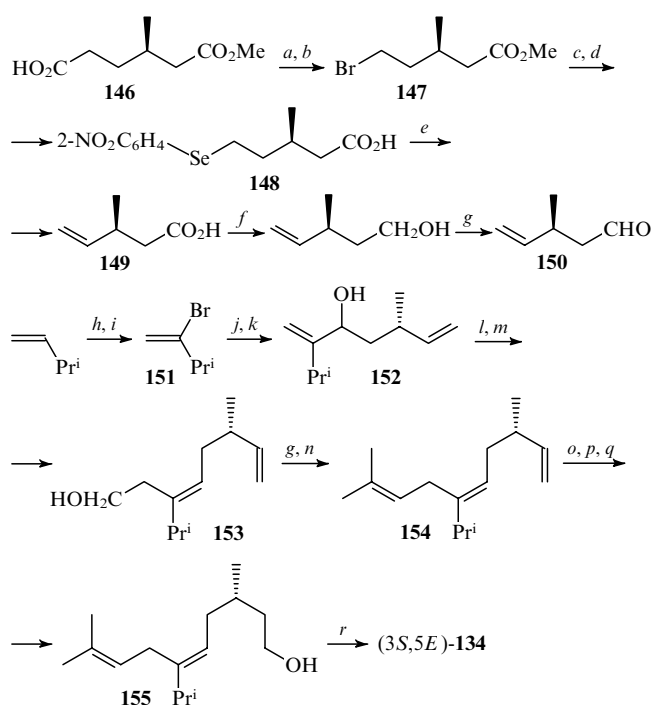
Mori and coworkers⁷² established the absolute configuration of the C(3) centre in the acetate **134** and performed the synthesis of (3S,5E)-**134** exhibiting the high attractant activity. For this purpose, chiral monoester (R)-**146**, which was synthesised from (R)-citronellic acid, was used as the starting compound. The Hunsdiecker reaction of the monoester (R)-**146** afforded bromide **147**, which was transformed into acid **149** *via* selenide **148**. The acid **149** was smoothly converted into aldehyde **150**. The reaction of the aldehyde **150** with an organomagnesium compound prepared from bromide **151** gave rise to alcohol **152**, which was subjected to the Still rearrangement. The alcohol **153** containing the trisubstituted alkene fragment was obtained with a stereoselectivity of > 95%. The reaction of an aldehyde prepared from **153** with isopropylidenetriphenylphosphorane afforded triene **154**. Hydroboration–oxidation of the terminal double bond in the triene **154** followed by acetylation of the resulting alcohol **155** completed the synthesis of (3S,5E)-**134** (the total yield was 0.2%).

Later, Mori and Kuwahara⁷³ performed a more efficient synthesis of (3S,5E)-**134**. According to this scheme, the trisubstituted alkene fragment was also constructed by the Still rearrangement. The key intermediate, *viz.*, benzyloxy alcohol **156**, was prepared by the reaction of the organomagnesium derivative of the bromide **151** with aldehyde **157**. The latter was synthesised by the seven-step transformation of methyl (R)-citronellate [(R)-**158**]. The conversion of the benzyloxy alcohol **156** according to Still giving rise to benzyloxy alcohol **159**, oxidation of the latter and treatment of the resulting aldehyde with isopropylidenetriphenylphosphorane afforded benzyl ether **160**. The target acetate (3S,5E)-**134** was prepared from **160** in 7% total yield.

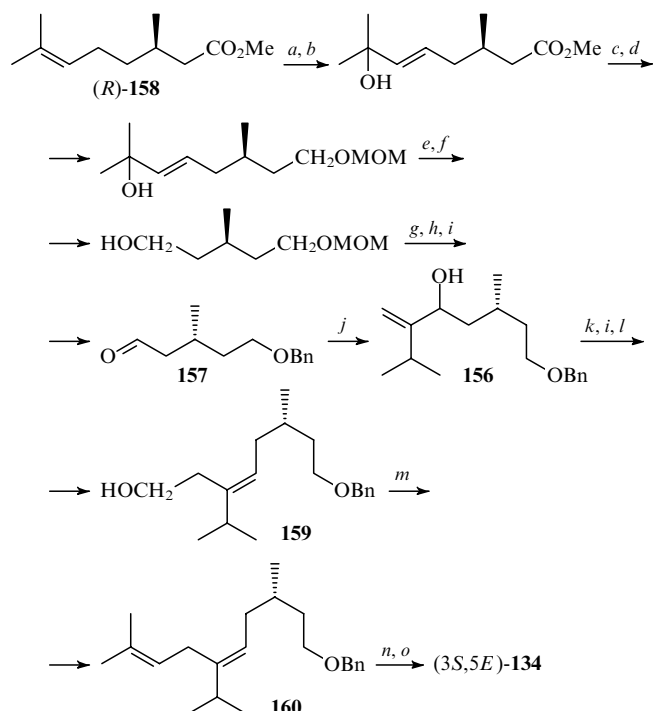
Scheme 1



(a) Mg, $\text{H}_2\text{C}=\text{CH}(\text{Pr}^i)\text{CHO}$; (b) $\text{MeC}(\text{OEt})_3$; (c) EtCO_2H , 135 °C; (d) MeMgI; (e) POCl_3 , Py; (f) 9-borabicyclo[3.3.1]nonane (9-BBN); (g) NaOH; (h) H_2O_2 ; (i) Ac_2O , Py; (j) LiAlH_4 ; (k) DHP, TsOH; (l) MCPBA; (m) Ph_2PLi , MeI; (n) H_3O^+ ; (o) PDC, DMF; (p) CH_2N_2 .



(a) Ag₂O; (b) Br₂; (c) 2-NO₂C₆H₄SeCN, NaBH₄; (d) NaOH, Δ; (e) H₂O₂; (f) LiAlH₄; (g) PDC, CH₂Cl₂; (h) Br₂; (i) 2,5-Me₂C₆H₃OH, NaH; (j) Mg; (k) **150**, THF; (l) KH, Bu₃SnCH₂I; (m) BuLi; (n) Ph₃P=CMe₂; (o) 9-BBN; (p) NaOH; (q) H₂O₂; (r) Ac₂O, Py.

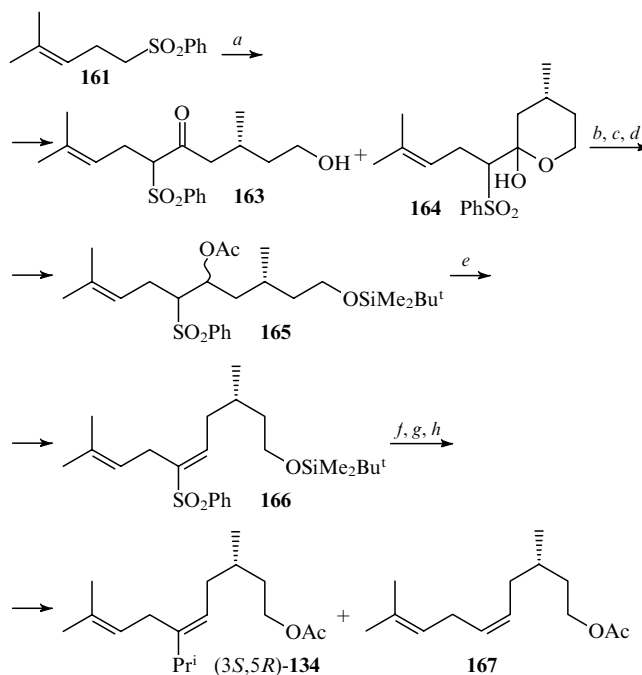


(a) (PhSe)₂, H₂O₂; (b) Bu₃O₂; (c) LiAlH₄; (d) NaH, MeOCH₂Cl (MOMCl); (e) O₃, NaHCO₃, MeOH; (f) LiAlH₄; (g) NaH, BnCl; (h) TsOH, MeOH; (i) PDC, CH₂Cl₂; (j) H₂C=C(Prⁱ)MgBr; (k) KH, Bu₃SnCH₂I; (l) BuLi; (m) Ph₃P=C(Me)₂; (n) Li/NH₃; (o) Ac₂O, Py.

Simultaneously, Mori and Kuwahara⁷³ prepared (3*R*,5*E*)-**134** in 10% total yield. Bioassays demonstrated that only the (3*S*)-enantiomer exhibited the attractant activity.^{73, 74}

Although Mori and coworkers^{70, 72, 73} succeeded in performing stereoselective synthesis of (3*S*,5*E*)-**134**, the synthetic schemes involved many steps and, as a result, the target compound was prepared in low yield. Later, more efficient syntheses of the acetate (5*E*)-**134** were performed.^{75–77}

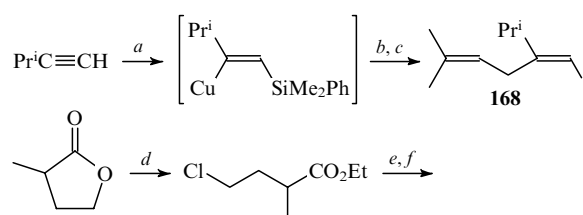
Julia and coworkers⁷⁵ constructed the chiral fragment in the acetate (5*E*)-**134** by the reaction of an anion generated from sulfone **161** with (3*R*)-methylvalerolactone (**162**). When treated with *tert*-butyldimethylchlorosilane, the resulting mixture of hydroxy oxo sulfone **163** and hemiketal **164** was quantitatively converted into the silyl derivative of hydroxy oxo sulfone **163**. Reduction of the carbonyl group in **163** followed by acetylation of a mixture of the resulting alcohols afforded a mixture of acetates **165**. Elimination of AcOH from the acetates **165** resulted in sulfone **166** containing an admixture (< 2%) of the (5*Z*)-isomer.

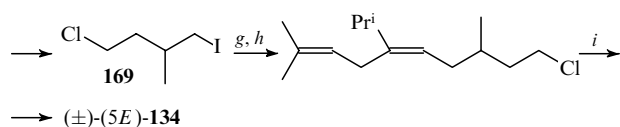


(a) BuLi, **162**; (b) LDA, Me₂Bu^tSiCl; (c) NaBH₄; (d) Ac₂O, dimethylaminopyridine (DMAP), Py; (e) NaOH; (f) PrⁱMgBr, FeCl₃; (g) Bu₄NF; (h) Ac₂O, Py.

The reaction of the sulfone **166** with PrⁱMgBr in the presence of FeCl₃ afforded, like other analogous reactions studied previously,⁷⁸ a 1 : 1 mixture of products of replacement and elimination of the sulfonyl group. After removal of the silyl protection, chromatographic separation of the resulting mixture of the acetates (3*S*,5*E*)-**134** and **167**, (3*S*,5*E*)-**134** was isolated in 17.2% total yield.

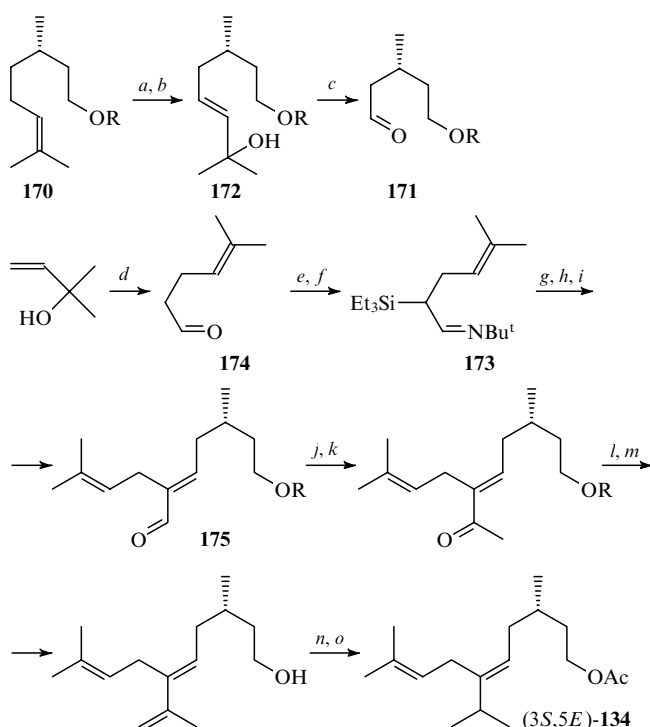
Millar⁷⁶ constructed the trisubstituted alkene fragment in the compound (5*E*)-**134** based on the above-mentioned highly stereoselective addition of cuprates to alkynes. Thus successive treatment of 3-methylbut-1-yne with (PhMe₂Si)₂CuLi (Ref. 79) and 3-methylbut-2-enyl bromide gave rise to vinylsilane containing 16% of the S_N2'-addition product. This mixture was converted into the corresponding iodides. Flash chromatography of the latter afforded iodide **168** in 39% total yield. This iodide was transformed into the target acetate (±)-(5*E*)-**134** by cross-coupling with an organozinc reagent synthesised from iodide **169**. The reaction product was converted into the target acetate (±)-(5*E*)-**134** (the total yield was ~ 16%).





(a) 2 equiv. of PhMe_2SiLi , CuCN , THF; (b) $\text{BrCH}_2\text{CH}=\text{CMe}_2$; (c) I_2 ; (d) HCl , EtOH ; (e) LiAlH_4 ; (f) $\text{I}_2 \cdot \text{Ph}_3\text{P}$, imidazole; (g) Zn , THF; (h) **168**, $(\text{Ph}_3\text{P})_4\text{Pd}$; (i) NaOAc , HMPA.

The pheromone (3*S*,5*E*)-**134** was also synthesised⁷⁷ starting from (*S*)-citronellyl pivalate (**170**). The highly stereoselective construction of the trisubstituted alkene fragment took advantage of thermodynamic predominance of the (*E*)-isomers of α,β -disubstituted acroleins,⁵³ *i.e.*, it is based on the approach used previously⁵⁰ in the synthesis of the pheromone of the California red scale **72**. The first synthon, *viz.*, aldehyde **171**, was prepared from the ester **170** by oxidation of its phenylselenenyl derivative with di-*tert*-butyl peroxide.



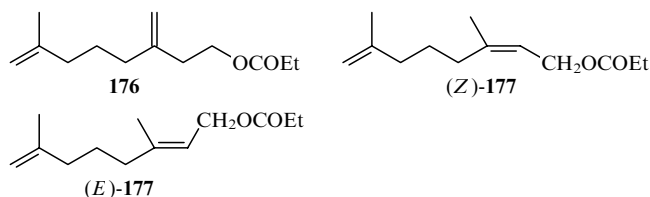
$\text{R} = \text{COBu}^t$; (a) $(\text{PhSe})_2$, H_2O_2 ; (b) Bu^tO_2 ; (c) O_3 , -78°C ; (d) $\text{EtOCH}=\text{CH}_2$, H_3PO_4 , 150°C ; (e) Bu^tNH_2 , 4 Å molecular sieves; (f) LDA , Et_3SiCl ; (g) Bu^tLi , **171**; (h) $\text{CF}_3\text{CO}_2\text{H}$, H_2O ; (i) $\text{C}_5\text{H}_5\text{N} \cdot \text{HCl}$; (j) MeMgI ; (k) $(\text{COCl})_2$, DMSO , Et_3N ; (l) $\text{Ph}_3\text{P}=\text{CH}_2$; (m) Bu_2AlH ; (n) H_2 , $(\text{Ph}_3\text{P})_3\text{RhCl}$; (o) Ac_2O , Et_3N .

Subsequent ozonolysis of the resulting tertiary alcohol **172** afforded the aldehyde **171**. The second synthon, *viz.*, silylated imine **173**, was prepared by condensation of 2-methylbut-3-en-2-ol with ethyl vinyl ether followed by successive treatment of the resulting aldehyde **174** with Bu^tNH_2 and Et_3SiCl . Condensation of the imine **173** with the aldehyde **171** under conditions used previously⁵⁰ in the synthesis of the pheromone **72** yielded acrolein **175**, which virtually did not contain the (*Z*)-isomer. The carbonyl group in the aldehyde **175** was converted into the isopropyl fragment in six steps. The target acetate (3*S*,5*E*)-**134** was prepared in 25% total yield. This is the best result obtained in the synthesis of the sex pheromone of the yellow scale.

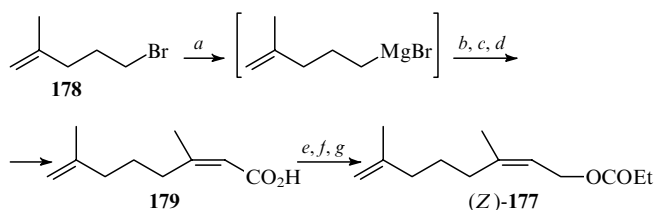
d. Sex pheromone of the San Jose scale

Almost simultaneously with the pheromone of the yellow scale, the female-produced sex pheromone of the San Jose scale *Quadraspidiotus perniciosus*, which is a widespread polyphagous pest of fruit and decorative trees, was isolated.⁸⁰ Two major components

of this pheromone, *viz.*, esters **176** and (*Z*)-**177**, were identified by physicochemical methods. More recently,⁸¹ the ester (*E*)-**177** was also found. It was demonstrated that the pheromone contains these components in a ratio of 47.55:47.75:4.70.⁸¹ Each of these components exhibits approximately the same biological activity.



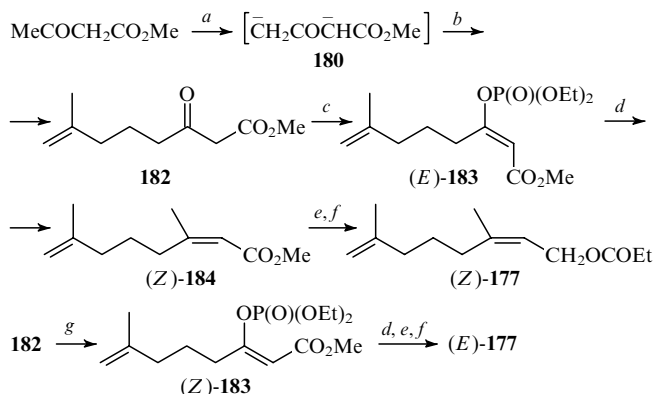
The ester (*Z*)-**177** was synthesised for the first time⁸² with the use of the above-mentioned highly stereoselective addition of dialkyl cuprates to alkynes in the key step of the construction of the (*Z*)-trisubstituted alkene fragment.



(a) Mg ; (b) $\text{CuBr} \cdot \text{Me}_2\text{S}$; (c) $\text{HC}\equiv\text{CMe}$; (d) CO_2 , $(\text{EtO})_3\text{P}$, HMPA; (e) CH_2N_2 ; (f) Bu_2AlH ; (g) $(\text{EtCO})_2\text{O}$, Py .

The reaction of cuprate obtained from the magnesium derivative of bromide **178** with propyne proceeded as *cis*-addition. Treatment of the reaction mixture with CO_2 afforded (*Z*)-acid **179**. The latter was converted into the target pheromone (*Z*)-**177** in 29% total yield using standard procedures.

Alderice *et al.*⁸³ synthesised the ester (*Z*)-**177** using the stereoselective conversion of enol phosphates of β -oxo esters into (*Z*)-trisubstituted α,β -unsaturated esters.⁸⁴

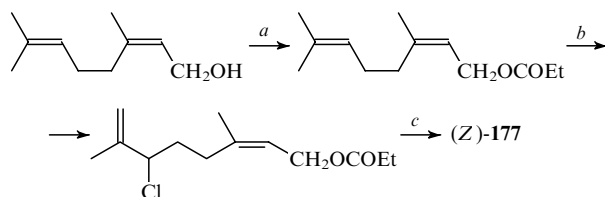


(a) NaH , BuLi ; (b) $\text{H}_2\text{C}=\text{CH}(\text{Me})\text{CH}_2\text{CH}_2\text{OTs}$ (**181**); (c) $(\text{EtO})_2\text{P}(\text{O})\text{Cl}$, Et_3N ; (d) MeMgCl , MeCu ; (e) Bu_2AlH ; (f) $(\text{EtCO})_2\text{O}$, Py ; (g) $(\text{EtO})_2\text{P}(\text{O})\text{Cl}$, NaH .

Thus dianion **180** generated from methyl acetoacetate underwent smooth alkylation under the action of tosylate **181** to form β -oxo acid ester **182**. The latter was converted into enol phosphate (*E*)-**183**. Treatment of (*E*)-**183** with MeMgCl in the presence of a catalytic amount of MeCu afforded ester (*Z*)-**184**, which was transformed into the target pheromone (*Z*)-**177** through the corresponding alcohol in ~40% total yield. Deprotonation of the oxo ester **182** with NaH instead of Et_3N afforded the (*Z*)-enol phosphate **183**. The latter was converted into the component of the pheromone of the San Jose scale, *viz.*, the propionate (*E*)-**177**, in three steps.

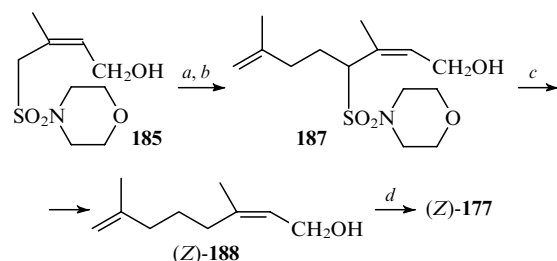
Nerol is a convenient starting compound for the synthesis of the ester (*Z*)-**177**. However, isomerisation of the $\text{C}(6)=\text{C}(7)$ double bond appeared to be a difficult problem. Only after several

unsuccessful attempts,⁸⁵ an efficient reagent for this isomerisation, *viz.*, *tert*-butyl hypochlorite, was found.^{86,87} The propionate (*Z*)-**177** was synthesised according to this scheme in three steps in 40% total yield.



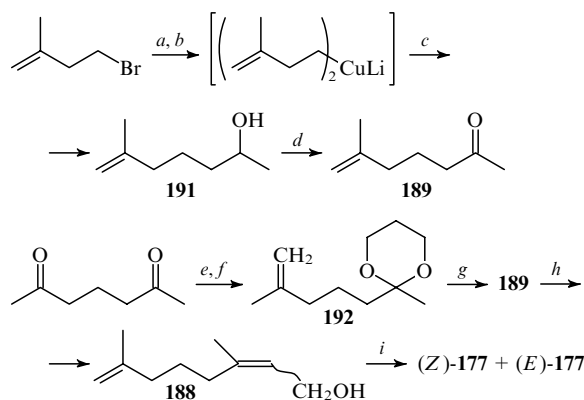
(a) (EtCO)₂O, Py; (b) Bu^tOCl, SiO₂; (c) NaBH₄, LiI.

Moiseenkov *et al.*⁸⁸ synthesised the propionate (*Z*)-**177** starting from isoprenoid (*Z*)-hydroxy sulfonamide **185**.⁸⁹ The synthetic scheme involved alkylation of the sulfonamide **185** with 3-methylbut-3-enyl iodide **186** to form sulfonamide **187** and reductive desulfurization of the latter in the presence of dibenzo-18-crown-6 (DB-18-C-6). The reaction proceeded virtually without migration of the C=C bond to form alcohol (*Z*)-**188**, which was converted into the propionate (*Z*)-**177** in 51% total yield.



(a) BuLi, THF; (b) H₂C=C(Me)(CH₂)₂I (**186**); (c) Na/NH₃, C₆H₁₄, DB-18-C-6; (d) (EtCO)₂O, Py.

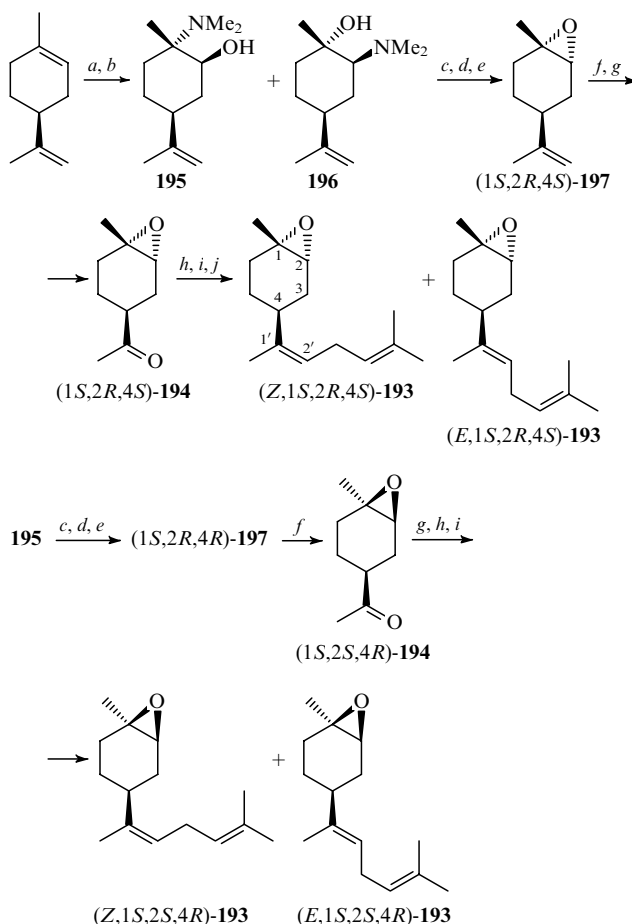
A mixture of propionates (*Z*)- and (*E*)-**177** was synthesised by Chinese chemists.^{90–92} The synthesis involved the Wittig reaction of ketone **189** with ylide generated from phosphonium salt **190** followed by the conversion of the resulting mixture of alcohols **188** into a mixture of propionates (*Z*)- and (*E*)-**177**. The key intermediate, *viz.*, the ketone **189**, was prepared in two ways. The first route^{90,91} involved oxidation of alcohol **191** formed in the reaction of diisopentenyl cuprate with propylene oxide. The second route⁹² involved the conversion of heptane-2,6-dione monoketal into the ketone **189** *via* ketal **192**.



(a) Li; (b) CuI; (c) $\text{Me} \begin{array}{c} \diagup \diagdown \\ \text{O} \end{array}$; (d) PCC, CH₂Cl₂; (e) BnO(CH₂)₃OH on a polymeric support; (f) Ph₃P=CH₂; (g) H₃O⁺; (h) (Ph₃P⁺CH₂CH₂OH)Cl[–] (**190**), B[–]; (i) (EtCO)₂O, Py.

2. Synthesis of the male-produced sex pheromone of the southern green stinkbug *Nezara viridula*

The southern green stinkbug *Nezara viridula* is a pest of cotton, citrus, cereal and vegetable crops, which is widely distributed in tropical and subtropical regions. The first data on the structure of the male-produced sex pheromone of *N. viridula* were published in 1971.⁹³ However, its major component was isolated only in 1987.⁹⁴ Based on the results of physicochemical studies, the structure of epoxybisabolene (**193**) was assigned to this component. With the aim of establishing the stereochemistry of the natural pheromone, eight of its isomers were synthesised⁹⁴ starting from (*R*)- and (*S*)-limonenes using the modified Julia procedure⁷⁵ in the step of construction of the trisubstituted alkene fragment.⁹⁵ The approach used in the cited study⁹⁴ is exemplified in the syntheses of the (*Z*)- and (*E*)-isomers of (1*S*,2*R*,4*S*)-**193** considered below. The necessary key intermediate, *viz.*, epoxy ketone **194**, was prepared in the individual state with the use of a reaction sequence involving epoxidation of (*S*)-limonene and conversion of the resulting mixture of α - and β -epoxides into a mixture of amino alcohols **195** and **196**. The latter compounds were converted into the corresponding tosylates and separated by chromatography.

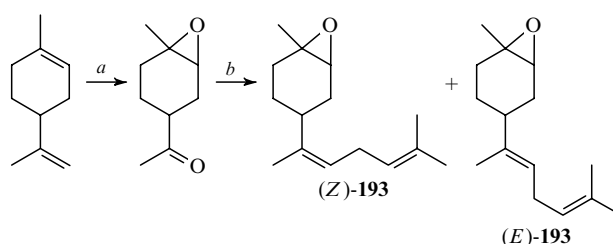


(a) MCPBA; (b) Me₂NH, H₂O; (c) TsCl, Py; (d) MeI; (e) KOH; (f) O₃, CH₂Cl₂; (g) Ph₃P; (h) Me₂C=CH(CH₂)₂SO₂Ph (**198**), BuLi; (i) PhCOCl, Py; (j) Na/Hg, THF, MeOH.

Amino tosylate corresponding to the amino alcohol **196** was transformed into the quaternary ammonium salt and then into individual epoxide (1*S*,2*R*,4*S*)-**197**. Ozonation of the double bond in (1*S*,2*R*,4*S*)-**197** followed by the reaction of the resulting epoxy ketone (1*S*,2*R*,4*S*)-**194** with deprotonated sulfone **198** afforded β -hydroxy sulfone. The latter was converted into benzoate. Subsequent reductive elimination gave rise to a 1:1 mixture of the (*Z*)- and (*E*)-isomers of epoxybisabolene (1*S*,2*R*,4*S*)-**193**. The individual isomers were isolated by HPLC. The (*Z*)- and (*E*)-iso-

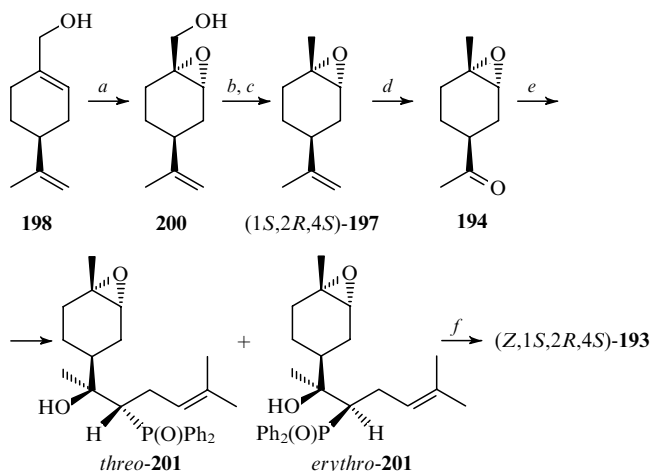
mers of epoxybisabolene (1*S*,2*S*,4*R*)-**193** were prepared analogously from epoxy ketone (1*S*,3*S*,4*R*)-**194**. Four other isomeric epoxybisabolenes were prepared starting from (*R*)-limonene. Based on comparison of the physicochemical characteristics of the isomers synthesised with those of the male-produced pheromone of stinkbugs of the Brazilian population, it was reliably established that the pheromone is epoxybisabolene (Z,1*S*,3*R*,4*S*)-**193**. Bioassays demonstrated that only this isomer was attractive to *N. viridula* females.

Later, it was shown^{96–99} that other isomers of epoxybisabolene **193** with the (*Z*)-configuration of the C(5)=C(6) double bond as well as (*Z*)-bisabolene are sex pheromones of stinkbugs from other regions. The ratio between the components in the pheromone mixture varies depending on the habitat. In this connection, synthesis of racemic epoxybisabolene (Z)-**193** starting from racemic limonene (patented by Mori *et al.*¹⁰⁰) is of interest. The individual epoxybisabolene (Z)-**193** was isolated from a mixture with the (*E*)-isomer by chromatography.



(a) MCPBA; (b) $\text{Ph}_3\text{P}=\text{CHCH}_2\text{CH}=\text{CMe}_2$.

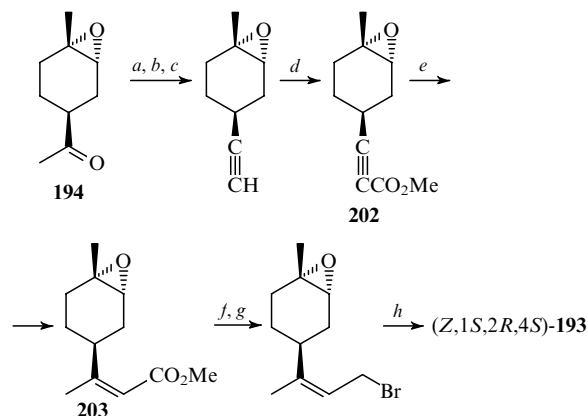
The major component of all pheromone mixtures of the southern green stinkbug, *viz.*, epoxybisabolene (Z,1*S*,2*R*,4*S*)-**193**, was synthesised¹⁰¹ from commercially available perillyl alcohol **198**. The key step of this scheme involved the Horner–Emmons reaction of the ketone **194** with phosphine oxide **199**. Epoxidation of perillyl alcohol **198** according to Sharpless afforded hydroxy epoxide **200**. The hydroxymethyl group of **200** was reduced to the methyl group through the corresponding mesylate. The resulting epoxide **197** was converted into the corresponding epoxy ketone **194** (the total yield was 47%). The reaction of the latter with an anion generated from the phosphine oxide **199** gave rise to a mixture of *erythro*- and *threo*-phosphine oxides **201**. The former was isolated by chromatography from a mixture with (*E*)-epoxybisabolene, which was formed due to decomposition of the unstable *threo*-**201**, and was converted into the epoxybisabolene (Z,1*S*,2*R*,4*S*)-**193** (the total yield was 18%).



(a) (D)-(–)-tartaric acid, $\text{Ti}(\text{OPr})_4$, $\text{Bu}^t\text{O}_2\text{H}$; (b) MeSO_2Cl , Py; (c) LiAlH_4 ; (d) KMnO_4 , DB-18-C-6, CH_2Cl_2 ; (e) $\text{Me}_2\text{C}=\text{CH}(\text{CH}_2)_2\text{P}(\text{O})\text{Ph}_2$ (**199**), BuLi; (f) NaH, DMF.

Efficient syntheses of the isomers (Z,1*S*,2*R*,4*S*)-, (Z,1*S*,2*S*,4*R*)-, (Z,1*R*,2*S*,4*R*)- and (Z,1*R*,2*R*,4*S*)-**193** were carried

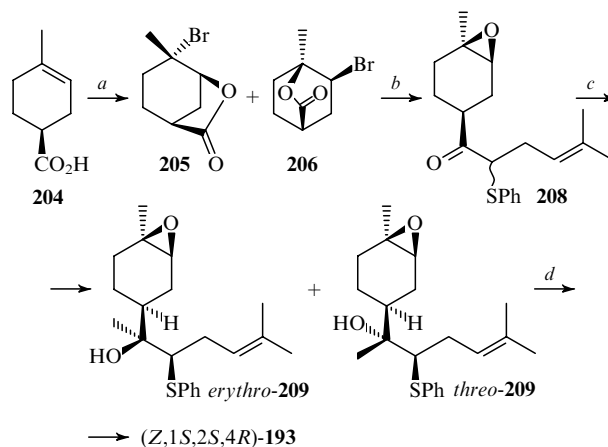
out¹⁰² starting from the commercially available mixture of α - and β -epoxides of (*S*)- and (*R*)-limonenes. The (*Z*)-trisubstituted alkene fragment was constructed using the highly stereoselective *cis*-addition of dialkyl lithium cuprates to acetylenecarboxylic esters. The scheme of the synthesis is exemplified below in the preparation of the isomer (Z,1*S*,2*R*,4*S*)-**193**.



(a) LDA; (b) $(\text{EtO})_2\text{P}(\text{O})\text{Cl}$; (c) 2.5 equiv. of LDA; (d) BuLi, ClCO_2Me ; (e) Me_2CuLi ; (f) Bu_2^tAlH ; (g) CBr_4 , PPh₃; (h) Bu^tLi, $\text{Me}_2\text{C}=\text{CHBr}$.

Substituted acetylenecarboxylic ester **202** was prepared from the epoxy ketone (1*S*,2*R*,4*S*)-**194** in four steps. The addition of dimethyl lithium cuprate to the ester **202** afforded ester (2*Z*)-**203**. The latter was transformed into (Z,1*S*,2*R*,4*S*)-**193** in 24% total yield according to standard procedures. Analogously, the isomer (Z,1*S*,2*S*,4*R*)-**193** was prepared from the ketone (1*S*,2*S*,4*R*)-**194** and the isomers (Z,1*R*,2*R*,4*R*)- and (Z,1*R*,2*R*,4*S*)-**193** were prepared from α - and β -epoxides of (*R*)-limonene, respectively.

(Z,1*S*,2*S*,4*R*)-Epoxybisabolene was also synthesised¹⁰³ starting from acid **204**, which was prepared by the asymmetric Diels–Alder reaction.¹⁰⁴ Bromolactonisation of the acid **204** gave rise to a mixture of bromo lactones **205** and **206**. Treatment of this mixture with 4-methyl-1-phenylthiopent-3-enyllithium (**207**) afforded phenylthio ketone **208** in high yield. The reaction of the compound **208** with MeLi gave rise to a mixture of *threo*- and *erythro*-hydroxy sulfides (**209**) separated by flash chromatography. Treatment of *threo*-**209** with P_2I_4 in the presence of Et_3N produced the target epoxybisabolene **193** in a total yield of 18% with respect to the acid **204**.



(a) NBS, Na_2CO_3 ; (b) $\text{Me}_2\text{C}=\text{CHCH}_2\text{CH}(\text{Li})\text{SPh}$ (**207**); (c) MeLi; (d) P_2I_4 , Et_3N , CH_2Cl_2 .

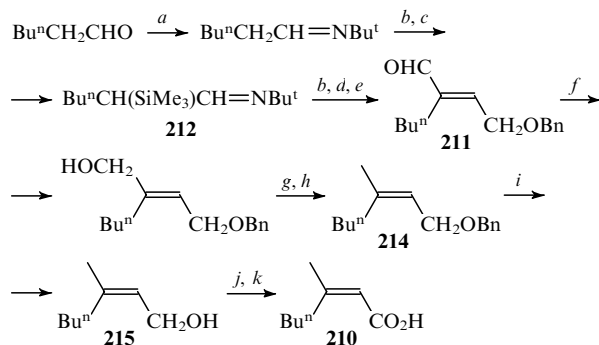
3. Synthesis of the sex pheromones of the dry bean beetles *Callosobruchus analis* and *C. maculatus*

The female-produced sex pheromone of the dry bean beetle *Callosobruchus analis* was isolated in 1991.¹⁰⁵ Based on the data

of GLC-mass spectrometry, the structure of 3-methylheptenoic acid containing a double bond at position 2 or 3 was assigned to this pheromone. Comparison of the physicochemical properties of the pheromone isolated with those of authentic 3-methylheptenoic acids containing a double bond at different positions (which were synthesised by the Reformatsky, Wittig or Horner–Emmons reactions) demonstrated that the pheromone of *C. analis* females is 3-methylhept-(2*Z*)-enoic acid (**210**). Bioassays of isomeric 3-methylheptenoic acids demonstrated that 3-methylhept-(3*Z*)-enoic acid is also the attractant for males of the dry bean beetle *C. analis*. This acid was identified as the major component of the sex pheromone of the dry bean beetle *C. maculatus*.^{105, 106}

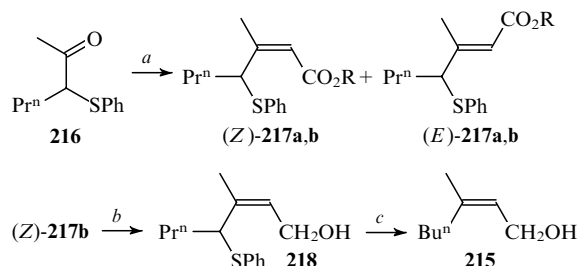
A highly stereoselective synthesis of 3-methylhept-(2*Z*)-enoic acid (**210**) was carried out according to two procedures. The first procedure¹⁰⁷ was based on the fact that the (*E*)-isomers of α,β -disubstituted acroleins are thermodynamically favourable.

In this scheme, the key intermediate was the (*E*)-isomer of substituted acrolein **211**, which was formed with a stereoselectivity of > 95% upon condensation of the trimethylsilyl derivative of *N*-*tert*-butylhexanimine (**212**) with glycolaldehyde benzyl ether (**213**).¹⁰⁷ Stereospecific reduction of the carbonyl group in the aldehyde **211** to the hydroxymethyl group and then to the methyl group *via* sulfate afforded benzyl ether **214**. Deprotection followed by oxidation of the resulting alcohol **215** gave rise to the acid **210** (the total yield was 12%).



(a) Bu^tNH_2 ; (b) LDA; (c) Me_3SiCl ; (d) OHCCH_2OBn (**213**); (e) H_3O^+ ; (f) NaBH_4 ; (g) $\text{Py} \cdot \text{SO}_3$; (h) LiAlH_4 ; (i) Li/NH_3 ; (j) MnO_2 ; (k) Ag_2O .

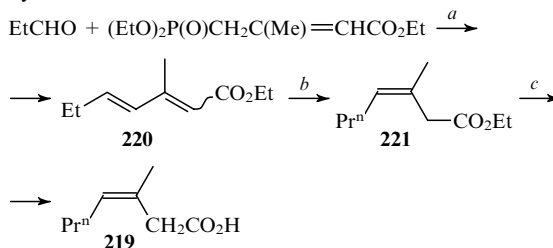
The second procedure¹⁰⁸ was based on our version of the highly stereoselective Peterson olefination^{109, 110} of methyl ketones. The method involves the introduction of a bulky phenylthio substituent at the C(3) atom. This substituent can be readily removed from the reaction product.



$\text{R} = \text{Me}$ (**a**), Bu^t (**b**); (a) $\text{Me}_3\text{SiCH}_2\text{CO}_2\text{R}$, LDA; (b) $[\text{AlH}_3]$; (c) Na/NH_3 , C_6H_{12} , DB-18-C-6.

Olefination of α -phenylthio ketone **216**, which was prepared according to Warren's method,¹¹¹ with alkyl trimethylsilylacetates afforded a mixture of 4-phenylthio esters (2*Z*)- and (2*E*)-**217a,b** (the ratios of the isomers were 92 : 8 and 85 : 15 for **217a** and **217b**, respectively). Reduction of the (*Z*)-ester **217b** isolated by chromatography with AlH_3 *in situ* gave rise to 4-phenylthio alcohol (2*Z*)-**218** desulfation of which afforded the alcohol **215** in 10.3% total yield. It should be noted that the yield of the alcohol **215** prepared according to the first procedure reached 26%.

3-Methylhept-(3*Z*)-enoic acid **219** was synthesised by Serebryakov and coworkers.^{112, 113} The key step of this scheme involved 1,4-*cis*-hydrogenation of conjugated dienes proposed by Frankel *et al.*⁵⁹



(a) KOH , 18-C-6, PhH ; (b) H_2 , $\text{Cr}(\text{CO})_6$, C_6H_{14} ; (c) KOH , HCl .

Condensation of propanal with triethyl 3-methyl-4-phosphonocrotonate under conditions of phase transfer catalysis afforded a mixture of esters (2*E*,4*E*)- and (2*Z*,4*E*)-**220**. Hydrogenation of this mixture over $\text{Cr}(\text{CO})_6$ gave rise to ester (3*Z*)-**221** with 99% purity. Saponification of the ester **221** under mild conditions produced the acid **219** in 11.4% total yield.

* * *

In conclusion, note that the synthesis of insect pheromones is a good 'proving ground' for new methods of organic chemistry. All the aforesaid refer in full measure both to stereoselective procedures for the construction of (*Z*)-trisubstituted $\text{C}=\text{C}$ bonds and to procedures for the construction of chiral synthons required for the preparation of pheromones of the group under consideration.

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Diacetylene: a candidate for industrially important reactions

I A Maretina, B A Trofimov

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Abstract. The review is devoted to industrially important syntheses based on diacetylene, a side product from electrocracking, oxidative pyrolysis of methane and plasmochemical synthesis of acetylene. Reactions of diacetylene and its derivatives with mono- and dinucleophilic reagents occurring in the chemisorption of diacetylene from industrial gases and resulting in stable reactive compounds which can be used as valuable intermediates for organic synthesis and pharmaceutical industry are described. Some specific features of diacetylene reactions in superbasic media are discussed. The bibliography includes 266 references.

I. Introduction

Preparation of chemical products on the basis of acetylene is one of the most promising trends in basic industrial organic synthesis. The interest in acetylene-related raw materials, which subsided considerably in 1955–1975, has now rekindled.¹ The reorientation towards coal and gas as valuable raw materials of the future and the development of new technologies for acetylene production from coal, *e.g.* using plasmochemical reactions, played a crucial role in the revision of the place of acetylene in organic synthesis.² The use of acetylene and its derivatives in small-tonnage production of sophisticated and expensive organic compounds holds especially great promise.^{1,2}

The classical studies by A E Favorsky and W Reppe have formed the basis for modern technologies of the chemistry of acetylene, *viz.*, vinylation, ethynylation and carbonylation reactions. A vast body of accumulated data on reactions of acetylene is documented in numerous monographs and reviews.^{1–40} On the other hand, some technological aspects of the chemistry of acetylene were obviously underestimated. This is particularly true of diacetylene (butadiyne) formed in the manufacture of

acetylene. As regards the potential utility of side products derived from acetylene and accompanying compounds (methylacetylene, allene, diacetylene, higher alkynes, phenylacetylene, *etc.*), diacetylene occupies the second place after the methylacetylene–allene fraction.

A significant contribution to the chemistry of diacetylene and its commercial application was made by Russian scientists belonging to the M F Shostakovskii^{3, 8, 11–32, 34} and A A Petrov^{36–40} scientific schools. The aim of the present review is to analyse and systematise the published data devoted to industrial syntheses based on diacetylene and to evaluate the prospects for the development of this branch of chemistry.

II. The problem of diacetylene utilisation

Despite the fact that many compounds of the diacetylene series (1,3-diynes) had been known since the XIX century, the development of the chemistry of these compounds began only after 1950³ when they were discovered in nature^{4,5} as well as among the products of electrocracking and oxidative pyrolysis of methane.⁶

Under industrial conditions, these two reactions yield, in addition to acetylene, some of its homologues and derivatives among which diacetylene constituting 5% of the whole manufacture of acetylene presents the greatest practical interest.¹

Utilisation of the accompanying diacetylene presents a serious problem for chemical technology. All industrial methods used for the isolation of acetylene are based on the sorption–desorption principle. Higher alkynes and diacetylene are extracted with the help of selective solvents, *e.g.*, anhydrous ammonia, cooled methanol, *N*-methylpyrrolidone, DMF.^{3,6}

The first solution to this problem was proposed and implemented at the oldest petrochemical plant ‘Chemische Werke Huls A.G.’⁴¹ Preparation of 1-methoxybut-1-en-3-yne as a 50% solution in methanol from accompanying diacetylene has been described.⁴² However, this method is not industrially acceptable because of extremely high diacetylene concentrations in the reactor. Labour protection laws currently in force in the Russian Federation prohibit the use of industrial technologies based on the use of material (gas or liquid) flows containing more than 10% of diacetylene.⁶ Therefore, problems of diacetylene extraction from gases produced by pyrolysis of hydrocarbon raw materials have

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received recently considerable attention, especially with regard to the safety of acetylene extraction due to the ability of diacetylene to undergo polymerisation and decomposition with explosion.

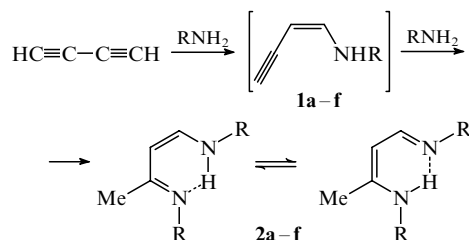
It should be noted in this connection that operations with diacetylene in manufacturing plants and in the laboratory belong to the category of particularly hazardous ones. It is therefore expedient to give due consideration to the vast experience accumulated in this area. The formation of a liquid phase in gas flows containing diacetylene is impermissible. The schemes of chemical conversion of diacetylene into practically valuable compounds should employ exclusively alkaline media, because the polymers formed under these conditions as side products are not hazardous. Manipulations with condensates or products prepared based on industrial diacetylene-containing gases differ substantially from those with pure diacetylene, since the polymerisation processes are more pronounced owing to the presence of higher 1,3-diynes. It is therefore preferable to prepare compounds which can easily be removed by distillation. It is rather difficult to isolate high-boiling products from such mixtures by conventional methods.

The technologies implemented in Russia were developed with due regard for safety for two main types of the processes, *viz.*, those in which liquid ammonia^{36,43,44} and *N*-methylpyrrolidone³⁷ were used as selective solvents. A possible approach to diacetylene utilisation is based on its ability to react with alcohols.^{36,37,41,42} The products of this reaction can be used in the synthesis of some aromatic and heterocyclic compounds (*e.g.*, monomers, dyes and drugs) as well in the production of plasticisers, herbicides, rubber vulcanisation accelerants, intermediates for electronic industry, broad-spectrum metal corrosion inhibitors, *etc.*^{36,37} Other conversions of diacetylene can be used in the synthesis of otherwise inaccessible heterocyclic compounds.^{38–40,45–47} All this makes diacetylene and its heterofunctional derivatives promising candidates for building blocks in the targeted synthesis of heterocyclic compounds.^{11–17,38–40,47}

Diacetylene most easily enters into reactions of nucleophilic addition with amines, alcohols and thiols, and high reactivities of the adducts make them promising reagents for practical purposes. In reactions with nucleophilic reagents, diacetylene behaves as a typical alkyne activated by an acceptor group,⁴⁷ *i.e.*, in this case the addition occurs at the terminal carbon atom of the acetylene bond, eventually resulting in the formation of 1-heteroalk-1-en-3-yne.

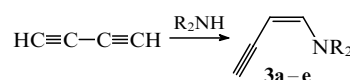
III. Reactions with amines

The addition of primary amines to diacetylene occurs readily at 30–40 °C in the absence of a catalyst. Usually, monoadducts of the type **1** cannot be isolated,⁴⁸ 1-*tert*-butylaminobut-1-en-3-yne (**1f**) being the only exception.⁴⁹ *N*-Alkyl(β -aminovinyl methyl)-ketimines or their tautomers, *e.g.*, *N*-alkyl-3-alkylaminocrotonal-dimines **2**, are the reaction products, which are formed in good yields.



R = Me (**a**), Et (**b**), Prⁿ (**c**), Prⁱ (**d**), Buⁿ (**e**), Bu^t (**f**).

According to the published data,^{48,49} the adducts **2** have *s*-Z-conformation which is stabilised by an intramolecular hydrogen bond. The reaction of diacetylene with secondary amines gives 1-dialkylaminobut-1-en-3-yne (**3**).^{3,47}

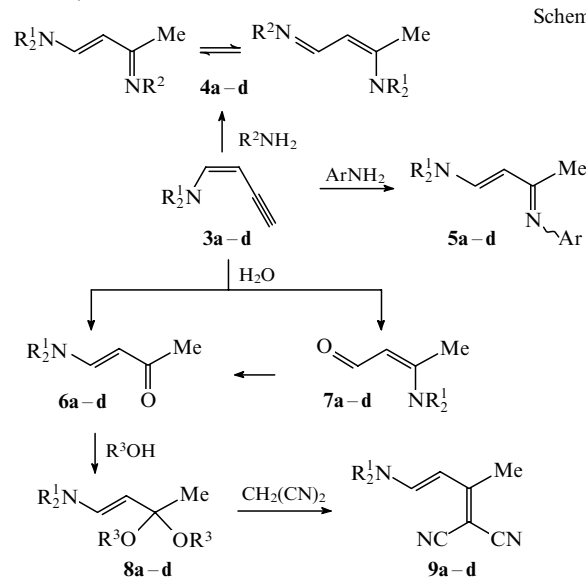


R = Me (**a**), Et (**b**), Prⁿ (**c**), Buⁿ (**d**); R₂N = N(CH₂)₂O (**e**).

The stereochemistry of the reaction of diacetylene with diethylamine in various solvents and at different temperatures resulting in the formation of the *Z*- and *E*-isomers **3b** has been studied.⁵⁰ The *E*:*Z* ratio increases with temperature. The *Z*-isomer prevails in acetonitrile, diethylamine and THF at 0–20 °C, whereas the *E*-isomer is predominantly formed in ethanol at 20 °C. The *Z* → *E* transition is observed only in the photolysis.

The kinetics of addition of secondary amines to diacetylene in dioxane at 20–80 °C corresponds to that of second-order reactions.⁵¹ The formation of compounds **3b,d** was monitored by UV-spectroscopy. The low values of activation entropy ($\Delta S^\ddagger = -55$ e.u.) and enthalpy ($\Delta H^\ddagger = 33.4$ kJ mol⁻¹) for the amine **3b** prompted a conclusion⁴⁷ that the addition occurs *via* intermediate products with considerable charge separation (bipolar ions). The final products result from intramolecular (*E*-isomers) or intermolecular (*Z*-isomers) proton transfer. The charge separation in the transition state favours both specific orientation of the amine and dioxane molecules and low values of activation entropy and enthalpy.⁴⁷

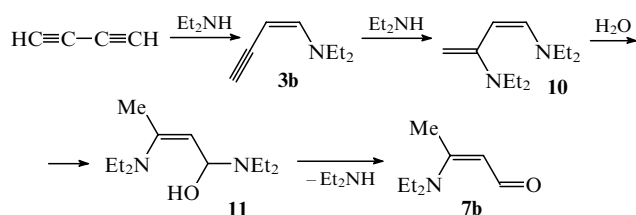
1-Dialkylaminobut-1-en-3-yne **3** with primary alkyl substituents react with primary amines to give potentially tautomeric aminocrotonal-dimines **4** due to the exchange of the amino groups. Reactions of compounds **3** with arylamines yield *C*-(2-dialkylaminovinyl)-*C*-methyl-*N*-(aryl)azomethines **5**.^{40,48} Depending on conditions, the hydration of amines **3** gives either 4-dialkylaminobut-3-en-2-ones **6**,^{3,46,52,53} or 3-dialkylaminobut-2-enals **7** (Scheme 1).⁴⁶



R¹ = Me (**a**), Et (**b**), Prⁿ (**c**), Buⁿ (**d**).

The addition of alcohols to enamino ketones **6** which is catalysed by bases gives the vinyllogues of aminoacetals **8**⁴⁰ which easily react with CH-acids, *e.g.*, malonodinitrile, to give the diene **9** (see Scheme 1).⁴⁰ Stepwise *C*-alkylation and hydrogenation of the amines **3** results in *N*-monosubstituted 1-aminoalkanes which represent valuable building blocks for the introduction of the 4-aminobutyl group.⁵⁴

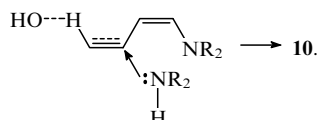
The reaction of diacetylene with an excess of diethylamine in dilute aqueous solutions of acetonitrile, ethanol or THF results in the diadduct, *viz.*, 1,3-bis(diethylamino)buta-1,3-diene (**10**); upon subsequent concentration of the reaction mixture, the latter is hydrated by a residual amount of water to be converted first into the hemiaminal **11** and then into the aldehyde **7b** following splitting-off of diethylamine.⁵⁵



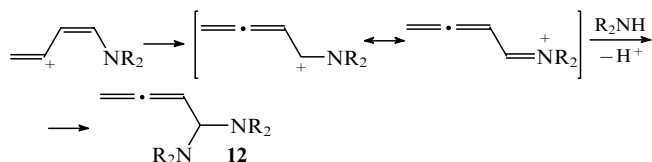
The reaction of the monoadduct **3b** with diethylamine is accompanied by the appearance of a band at 325 nm in the UV spectrum of the reaction mixture; its intensity increases with a simultaneous decrease in the intensity of the band at 275 nm corresponding to the original amine **3b**. After completion of the reaction, the UV spectrum contains only the former band corresponding to the product **10**.⁵⁵

The absorption band of the original enyne **3b** in the IR spectrum is shifted towards the low-frequency region; its intensity decreases simultaneously with the appearance of a band around 1580 cm^{-1} , which corresponds to the product **10** having Z-configuration.⁵⁵ The intensity of this band increases as the reaction proceeds further. The first diethylamine molecule adds to diacetylene in acetonitrile much faster than the second one.

Thus, the first step of the conversion of diacetylene into the bisadduct **10** is the rate-limiting step. The enhancing effect of the solvent is attributed to incomplete removal of water and hence to electrophilic catalysis by water molecules which attack the terminal atom of the ethynyl group:

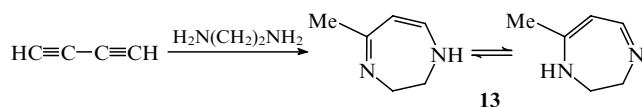


This transition state is in accord with the observed regioselectivity of the reaction and Z-configuration of the diene formed as well as with the high negative entropy and low activation energy of the reaction. The proton transfer and the addition of the nucleophile are synchronous processes and are accompanied by the migration of the positive charge to the α -carbon atom as might be expected. Otherwise, the allene **12** would be formed.⁵⁵

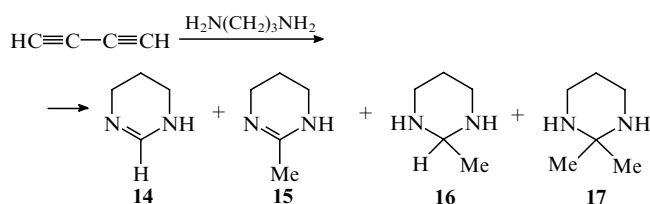


In aqueous solutions, the role of a nucleophile is played by water, which leads to the formation of the enamino ketone **6b**. The calculated rate constants for this reaction in aqueous THF are much lower than the rates of addition of the second diethylamine molecule to the amine **3b**, the enthalpy of activation is also lower. This attests to a concerted process and the involvement of the nucleophile in the limiting stage of both reactions, since water is a much weaker nucleophile than diethylamine.⁵⁵

1,2-Diaminoethane reacts with diacetylene to give a mixture of tautomers of 5-methyl-2,3-dihydro-1,4-diazepine (**13**).⁵⁶

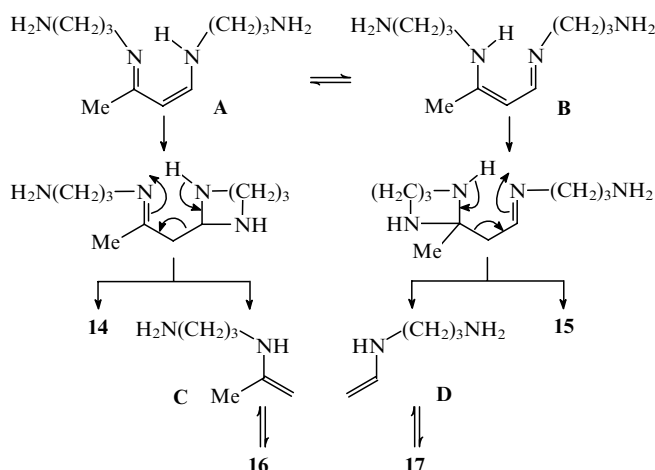


It was expected that the reaction of diacetylene and its homologues with 1,3-diaminopropane would give 1,2,3,4-tetrahydro-1,5-diazocine.⁵⁷ However, the reaction product represents a mixture of Δ^1 -tetrahydropyrimidine (**14**), 2-methyl- Δ^1 -tetrahydropyrimidine (**15**), 2-methyl- (**16**) and 2,2-dimethylhexahydropyrimidines (**17**).



This can be rationalised as the addition of two diamine molecules to one diyne molecule, resulting in the diadducts **A** and **B** which undergo further cyclisation and fragmentation in two directions (Scheme 2).

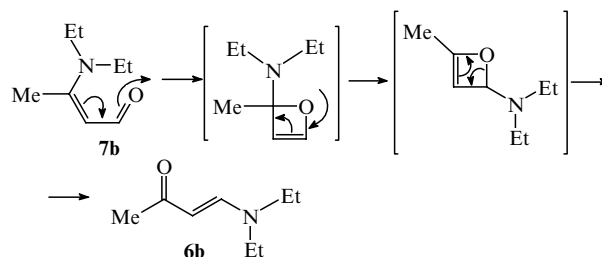
Scheme 2



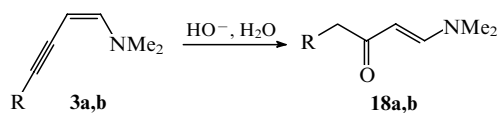
These results are similar to those obtained for the reaction of acetylacetone with 1,3-diaminopropane⁵⁷ and formally correspond to the scission of β -diketone derivatives.

As noted above, reactions of diacetylene with solutions of primary and secondary amines in aqueous ethanol produce enamino ketones **6**. It was found, however, that the physical constants of enamino ketones **6** thus prepared do not coincide with those prepared by amination of alkoxy ketones.⁵⁸ Later, this discrepancy was explained⁵⁹ by the formation of enamino aldehydes **7** along with enamino ketones **6** in reactions of diacetylene with solutions of amines in aqueous ethanol. Depending on the size of the alkyl substituents at the nitrogen atom and the concentration of the aqueous solution of alkali (3%–5%), the content of the aldehyde in the reaction mixture changes and may exceed 40% with respect to the ketone.⁵⁹ Thus if 3-dimethylaminobut-2-enal (**7a**) is formed only in trace amounts, the yields of the products **7b** and **7d** amount to 35% and 43%, respectively.⁵⁹

It is believed⁴⁶ that the formation of enamino ketones **6** from amines **3** can also occur *via* aldehydes **7**. With an increase in temperature, the ketone:aldehyde ratio increases.⁴⁶ Thermal isomerisation occurs quantitatively, probably, *via* the oxetene cycle. The aldehyde **7b** is fully isomerised into the ketone **6b** in 4 h at 150°C .



The addition of water to amines **3a,b** occurs easily in the presence of catalytic amounts of an alkali exclusively at position 3 and results in alkyl 2-dimethylaminovinyl ketones **18**.⁶⁰



R = Me (a), Et (b).

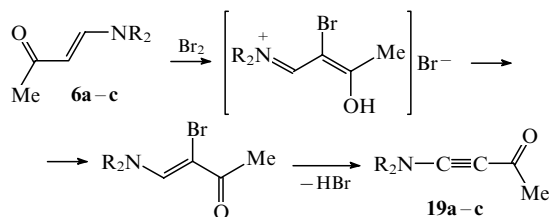
These conversions were used to develop a procedure for chemisorption of diacetylene by aqueous solutions of primary and secondary amines aimed at separation of diacetylene in the manufacture of acetylene by oxidative pyrolysis of methane.⁵⁹ This approach has been approved at the Yerevan Industrial Corporation 'Nairite' with both a real abgas[†] and a diacetylene-enriched condensate. Their compositions are shown in Table 1.⁵⁹ The presence of methane, nitrogen, ethylene and some other components in the abgas can be explained by the fact that diacetylene-containing gases are diluted with a cracking gas from which acetylene had previously been removed by absorption down to concentrations of $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$ (< 10 vol.%) which ensure their safety upon transportation.⁵⁹ Chemisorption of diacetylene is performed by a 25% aqueous solution of dimethylamine. The number of absorption plates and the design of the absorption apparatus ensure the absorption of 92%–94% of diacetylene at its average concentration of 6%–7%. The addition of dimethylamine to diacetylene occurs at 25–30 °C. Since this reaction is exothermic, the temperature of the reaction mass increases slowly to 50 °C.[‡] The amine **3a** formed in the first step was isolated from the reaction mixture in its individual state and characterised.⁵⁹

Table 1. The composition of abgases and their condensates.

Component	Content (vol.%)	
	in abgas	in condensate
Hydrogen	35–40	—
Methane	20–25	—
Nitrogen	7.0–11.0	—
Diacetylene	6.0–8.0	36–52
Ethylene	1.0–2.0	—
Methylacetylene	1.0–1.5	5.5–7.5
Benzene	1.0–1.5	5.0–7.0
Allene	0.5–1.0	3.5–5.5
Vinylacetylene	0.5–1.8	4.0–4.5

Then, the reaction mass is loaded into a reactor where the triple bond is hydrated at 60–65 °C. The ketones **6** formed are rather stable and convenient C₄-synthons for the synthesis of heterocyclic compounds.^{38–40}

1-Dialkylaminobut-3-yn-2-ones (**19**), which are promising reagents for the synthesis of heterocyclic compounds, are easily prepared by bromination and dehydrobromination of enaminone ketones **6**.^{62–67}

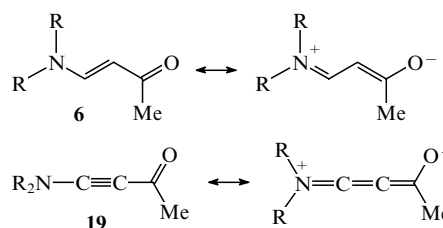


R = Me (a), Et (b), Prⁿ (c).

[†] Abgas is a technical term, which designates an absorption gas.

[‡] Among a vast array of products present in diacetylene as admixtures, vinylacetylene ranks second in reactivity after diacetylene. However, even this compound reacts with aqueous solutions of secondary amines at a detectable rate only at 100 °C in an autoclave.⁶¹

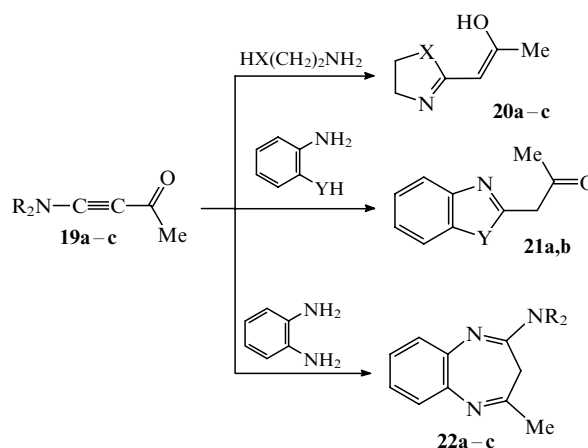
The structures and reactivities of enamino ketones **6**, **18** and ynamino ketones **19** were described in numerous publications.^{38, 39, 52, 62} The effects of substituents on the distribution of electron density in the molecules of en- and ynaminocarbonyl compounds were studied by ¹³C-NMR spectroscopy. These studies were aimed at the determination of spin-spin coupling constants (J_{CC}) ¹³C–¹³C at the double and triple bonds.⁶² The J_{CC} values were found to be significantly smaller than those calculated according to the additive scheme. This is due to delocalisation of the multiple bonds by direct polar conjugation, through the double (triple) bond involving the lone pair on the nitrogen atom and the π -system of the carbonyl fragment.



The contribution of the bipolar resonance form was estimated to be ~ 30% for enamino ketones **6** and exceeded 50% for ynamino ketones **19**.⁶² Comparison of chemical shifts in the ¹³C NMR spectra of carbon atoms at the triple bond of substituted ynamines with the corresponding values for the C atoms at the double bond of enamines led to a conclusion about cross-polarisation of the orthogonal π -system of the triple bond in ynamines containing acceptor groups.⁶²

This effect is manifested in the abnormally low shielding exerted by the dialkylamino group on the carbon atom of the multiple bond nearest to the nitrogen atom. Data on the structures of ynamino carbonyl compounds suggest that the conjugation of the donor and acceptor groups through the multiple bond (the so-called 'push-pull effect') strongly influences the distribution of electron density in the molecules and, as a consequence, their reactivities. As a result, these compounds acquire specific properties which differ radically from those of both ynamines and ketones containing a triple bond.⁴⁰

The behaviour of ynamino ketones **19** in cyclisation reactions differs from that of enamino ketones **6** and **18**.^{38, 39, 52} Whereas enamino carbonyl compounds typically 'deliver' three-carbon fragments in cyclisation,⁴⁰ ynamino ketones mostly react like simple ynamines, *i.e.*, with a twofold attack by bifunctional reagents on the carbon atoms of the triple bond (1,1-attack).⁵²



19, **22**: R = Me (a), Et (b), Prⁿ (c); **20**: X = NH (a), O (b), S (c);

21: Y = O (a), S (b).

Thus the reaction of ynamino ketones **19** with ethylenediamine, ethanolamine and 2-mercaptoethanol is accompanied by the elimination of the dialkylamino group and the formation of

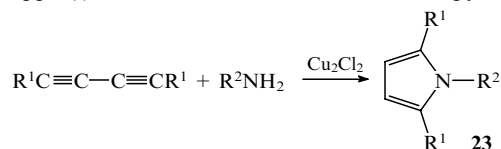
1-(4,5-dihydroimidazol-2-yl)prop-1-en-2-ol (**20a**), 1-(4,5-dihydro-oxazol-2-yl)prop-1-en-2-ol (**20b**) and 1-(4,5-dihydrothiazol-2-yl)prop-1-en-2-ol (**20c**), respectively, containing a fully enolised carbonyl fragment.^{68,69} The use of derivatives **20** as the X_{α} -inhibition factor⁷⁰ and anticonvulsants, *e.g.*, in the treatment of industrial electronic shock traumas, was described.⁷¹

The ynamino ketones **19** react with aromatic α,β -bifunctional reagents, *e.g.*, 2-aminophenol and 2-aminobenzenethiol, like ordinary ynamines^{72–76} to produce 1-(benzooxazol-2-yl)propan-2-one (**21a**) and 1-(benzothiazol-2-yl)propan-2-one (**21b**), respectively.^{77,78} Benzothiazole **21b** has been used in the synthesis of compounds for modulation of information signals⁷⁹ and pharmaceutical preparations against acidophilia, bronchial asthma, allergies,⁸⁰ diabetes and nephropathies.⁸¹ Benzothiazoles of the type **21b** manifest herbicidal activities⁸² and are used in the production of liquid-crystal compositions.⁸³

The cyclisation of ynamino ketones **19** with *o*-phenylenediamine results in 2-dialkylamino-4-methyl-3*H*-1,5-benzodiazepines **22**⁶⁹ in up to 83% yields.

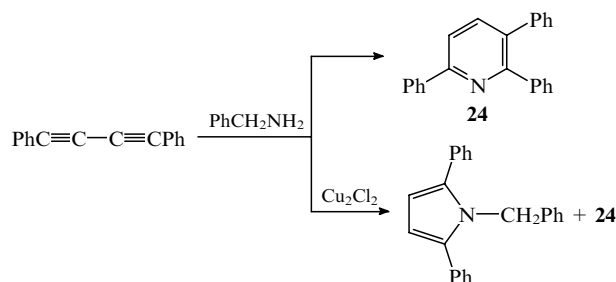
Photosensitive materials based on benzodiazepines **22** were patented.⁸⁴ Compounds of this class are used in the therapy of cholecystitis, gastritis⁸⁵ and meningitis⁸⁶ as well as squalene synthase inhibitors,⁸⁷ atypical neuroleptics⁸⁸ and fungicides against *Penicillium notatum*.⁸⁹ Thus, benzodiazepines of the type **22**, which have a wide range of practical applications, can also be synthesised from ynamino ketones.

The reaction of diacetylene with primary amines in the presence of copper(I) salts occurs as 1,4-addition and results in the formation of pyrrole or 1-alkylpyrroles.³ This reaction is carried out at 140–160 °C both in the absence of the solvent and in methanol, ethanol or DMF. In the latter case, the resulting pyrroles have a high degree of purity and are formed in higher yields. The reaction of ammonia and primary alkyl- and arylamines with disubstituted symmetrical 1,3-diynes in the presence of copper(I) chloride affords 1,2,5-trisubstituted pyrroles **23**.³



$R^1 = \text{H, Me, Et, Ph}; R^2 = \text{H, Me, Et, Bu}^n, \text{Ph}.$

According to Shostakovsky and Bogdanova,³ the role of a catalyst in this reaction consists in the formation of a non-polar π -complex with one of the triple bonds where the electron density is evenly distributed between both carbon atoms, which facilitates the interaction of the nucleophilic nitrogen with the fourth carbon atom of the conjugated diyne system. The smooth course of this reaction made it possible to develop a general scheme for the synthesis of substituted pyrroles.³ The practical significance of this class of compounds is documented in numerous monographs and reviews.^{13–16, 21, 29, 90–94} In the absence of a catalyst, the reaction of diphenylbutadiyne with benzylamine affords 2,3,6-triphenylpyridine (**24**) in 50% to 70% yield.⁹⁵

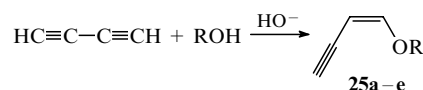


The specific feature of this reaction is that in the absence of a catalyst only pyridine **24** is formed; however, in the presence of Cu_2Cl_2 it proceeds simultaneously in two directions. This phe-

nomenon is interpreted by the ability of copper(I) chloride to coordinate both at the nitrogen atom and at the triple bond.⁹⁵

IV. Reactions with alcohols

The synthesis of 1-alkoxybut-1-en-3-yne **25** by the reaction of diacetylene with alcohols in the presence of a catalyst was described;³ however, the physical constants obtained by different authors differ.⁹⁶ This may be due to the difference in the ratios of *E*- and *Z*-isomers in the specimens prepared under different conditions or due to their contamination with products of further transformations of the ethers **25**.

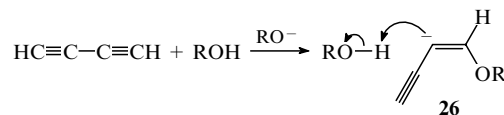


$R = \text{Me (a), Et (b), Pr}^n \text{ (c), Bu}^n \text{ (d), n-C}_5\text{H}_{11} \text{ (e).}$

The addition of methanol, ethanol, propan-1-ol, butan-1-ol, 2-methylpropan-2-ol, pentan-1-ol and hexan-1-ol to diacetylene has been studied under identical conditions at the alcohol: diacetylene ratio of 3:1 in the presence of catalytic amounts of KOH.⁹⁶ The content of *E*- and *Z*-isomers was determined on the basis of ^1H NMR spectroscopy and GLC data.

The ethers **25a,b** appeared to be pure *Z*-isomers; their homologues **25c,d** contained approximately equal amounts of the *E*-isomer (12.8%–13.3%), whereas compounds **25e,f** represented equimolar mixtures of *E*- and *Z*-isomers.⁹⁶ It is probable that the rule of *trans*-nucleophilic addition is observed only for lower alcohols. However, if the reaction mixture contains compounds capable of forming complexes with diacetylene, the above rule may not be observed as is the case even with the reaction of diacetylene with methanol, which gives up to 15% of the *E*-isomer with dioxane as a solvent.⁹⁶

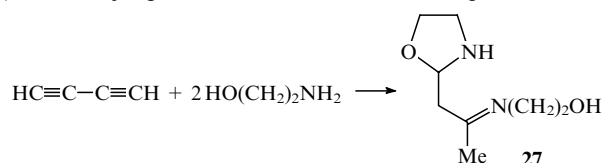
Kinetic studies of reactions of diacetylene with lower aliphatic alcohols in the presence of KOH were carried out using UV spectroscopy and GLC.^{97,98} The reaction of diacetylene with methanol (5 moles/mole of $HC\equiv C-C\equiv CH$) in the presence of KOH (0.22 moles/mole $HC\equiv C-C\equiv CH$) is described by an equation for a pseudo-unimolecular reaction with the activation enthalpy, $\Delta H^\ddagger$, of 87.8 kJ mol^{–1} and the activation entropy, $\Delta S^\ddagger$, of –19 e.u. The experimental results suggest⁴⁷ that the addition of the alkoxide ion to the terminal carbon atom of diacetylene followed by rapid protonation of the carbanionic intermediate **26** formed is the rate-limiting step of this reaction. *sp*²-Hybridisation of the carbon atom orbitals at the double bond and spatial hindrances created by bulky alkoxy and ethynyl groups direct the attack of the proton donor to the *trans*-position relative to the alkoxide ion.



UV spectroscopy and GLC were used to study⁹⁸ the kinetics of the reaction of diacetylene with methanol and ethanol under conditions close to the industrial ones,³⁷ in the presence of potassium hydroxide and sodium hydroxide at 50–73 °C and at a 1,3-diyne concentration of 2.5 mass %–10 mass %. Such a narrow temperature range can be explained by the fact that at lower temperatures diacetylene is predominantly polymerised due to the slow rate of the main reaction. At temperatures above 73 °C, this reaction proceeds further.⁹⁸ Since the rate of formation of the ether **25b** is proportional to the concentration of diacetylene in the solution, the reaction should be carried out at the maximally permissible (up to 10 mass %) concentration of $HC\equiv C-C\equiv CH$. The dependence of the rate constant for the formation of the ether **25b** on KOH concentration is more complex. With an increase in KOH concentration from 1% to 5%, the rate constant increases abruptly. Within the concentra-

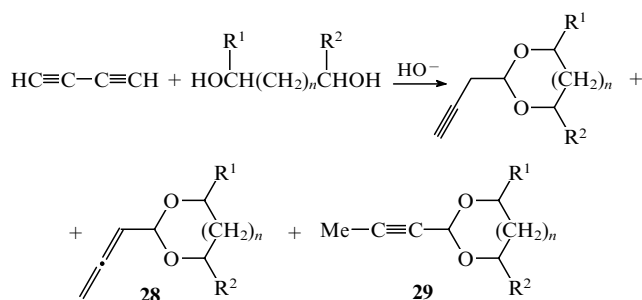
tion range of KOH from 5 mass % to 15 mass %, the reaction rate is not changed ($k_{\text{aver}} = 2.7\text{--}2.8 \text{ l mol}^{-1} \text{ s}^{-1}$, 60°C), but this drops drastically after further increase in the catalyst concentration.⁹⁸ This is ascribed to the simultaneous effect of several factors. At low concentrations of the catalyst, the increase in the reaction rate is mainly due to an increase in the concentration of the alkoxide ions responsible for this reaction. At 5 mass %–15 mass % of KOH, the concentration of alkoxide ions increases to such an extent that its fluctuations within the indicated range do not influence the reaction rate. At KOH concentrations above 15 mass %, the rate of side reactions increases drastically. From these data, it was concluded that the optimum concentration of KOH is 5 mass %.⁹⁸

When diacetylene was passed through a solution of monoethanolamine in benzene at 0°C , a crystalline product was formed which represents 2-[2-(2-hydroxyethyl)iminopropyl]oxazolidine (**27**) as can be judged from the ^1H and ^{13}C NMR spectral data.



This adduct of diacetylene with ethanolamine is used for stabilisation of biologically active substances in grass fodders.⁹⁹

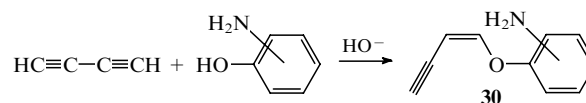
The binding of 1,2- and 1,3-diols to diacetylene was studied in the presence of catalytic amounts of alkali and resulted in a mixture of cyclic acetals of but-3-ynal, buta-2,3-dienal (**28**) and but-2-ynal (**29**); their ratio changed depending on experimental conditions.¹⁰⁰



$n = 0$: $\text{R}^1 = \text{R}^2 = \text{H}$; $n = 1$: $\text{R}^1 = \text{R}^2 = \text{H, Me}$, $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$.

Bifunctional derivatives of the aromatic series, such as *o*-, *m*- and *p*-aminophenols, add to diacetylene in the presence of alkalis

like ordinary alcohols, *i.e.*, through the hydroxy group, to give 1-aryloxybut-1-en-3-yne (**30**).¹⁰¹



Alcohols (glycols, amino alcohols) and phenols add to diacetylene under much milder conditions than to acetylene and vinylacetylene.^{37,98} The vinylation of lower alcohols with acetylene requires the use of superbasic media^{19,20,23,28,102} or heating up to $120\text{--}140^\circ\text{C}$, and their addition to vinylacetylene occurs at temperatures around 100°C , while the optimum temperature for the reaction of diacetylene with methanol in the presence of KOH (5 mass %) is as low as $72\text{--}73^\circ\text{C}$.^{37,98} This circumstance is extremely important because the substantial difference between the rates of the reaction of methylacetylene, vinylacetylene and diacetylene with lower aliphatic alcohols allows selective chemisorption of diacetylene from gas mixtures produced by acetylene-manufacturing plants^{36,37} which contain these particular hydrocarbons. Moreover, extraction of diacetylene from industrial gases allows implementation of technologies for industrial syntheses of isopropenylmethyl ether, acetone and acetylacetone based on the accompanying methylacetylene–allene fraction.¹

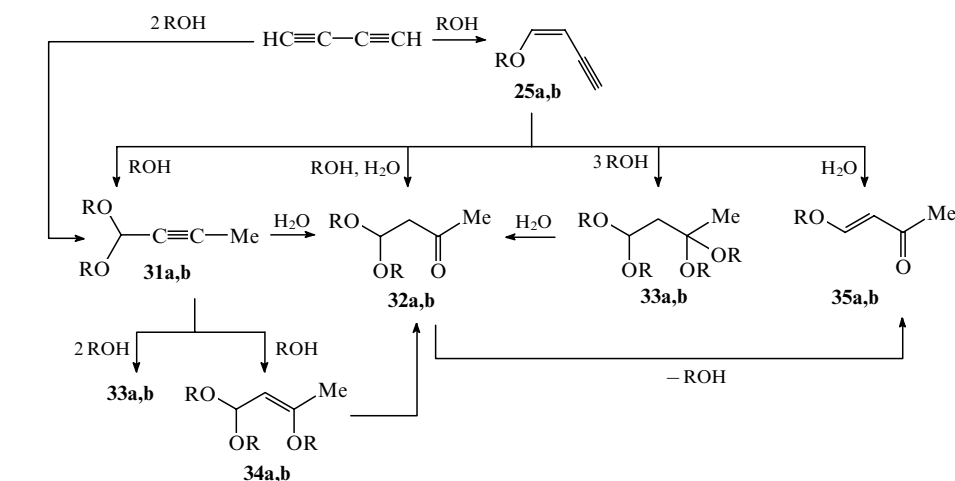
Numerous transformations of the ether **25a** have been described under conditions of alkaline and acid catalysis (Scheme 3).¹⁰³ Thus the addition of the second methanol molecule to the ether **25a** in the presence of an alkali results in 1,1-dimethoxybut-3-yne (**31a**). Its analogue, *viz.*, 1-methoxy-1-phenethoxybut-2-yne, is used in perfumery.¹⁰⁴

1,1-Dimethoxybutan-3-one (**32a**) is formed in 80% yield as a result of hydration of the triple bond of acetal **31a** under conditions of acid and mercury salt catalysis (H_2SO_4 , HgSO_4) in boiling aqueous methanol (see Scheme 3). The addition of an alcohol and water to the ether **25a** in the presence of an acid catalyst also results in the acetal **32a** in 85% yield.

1,1,3,3-Tetramethoxybutane (**33a**) and a small amount of 1,1,3-trimethoxybut-2-ene (**34a**) are formed under identical conditions but in the presence of dry methanol (3 equiv.). Upon mild hydrolysis at room temperature, this mixture is converted into the acetal **32a**; its complete hydrolysis yields 1,3,5-triacetylbenzene, which was first observed by Claisen.¹⁰⁵

Thus, the acetals **32a,b** appear to be the most convenient and stable intermediates prepared from diacetylene.¹⁰⁶

Thermal or catalytic elimination of methanol from the acetal **32a** gives 4-methoxybut-3-en-2-one (**35a**);¹⁰⁶ a mixture of compounds **32a** and **35a** (7 : 3) is formed in the presence of catalytic amounts of acids or alkalis. Its homologue **32b** ($\text{R} = \text{Et}$) yielded



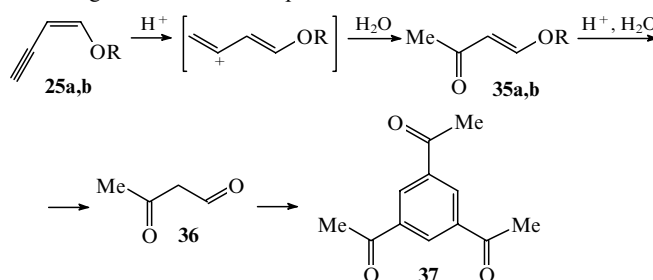
$\text{R} = \text{Me (a), Et (b)}$.

Scheme 3

an equilibrium mixture of **32b** and **35b** in a 7.5:2.5 ratio upon storage under conditions close to those employed in industry.⁹⁸

The structure of the ketone **35a** was studied in detail using UV, IR and NMR spectroscopy.¹⁰⁷ Analysis of thermochemical and ¹H NMR spectral data revealed¹⁰⁸ that this compound has *E*-configuration.¹⁰⁸

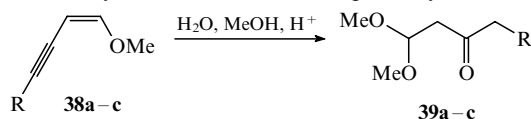
A kinetic analysis of acid-catalysed hydrolysis of the ethers **25a,b** by polarography^{109,110} provided support for the initial rapid hydration of the triple bond with subsequent slow protonation of ketones **35a,b**, which are further decomposed to 3-oxobutanal (**36**); the latter undergoes self-cyclisation into 1,3,5-triacetylbenzene (**37**). In water, the rate of this reaction is an order higher than in 25% aqueous DMF.



R = Me (a), Et (b).

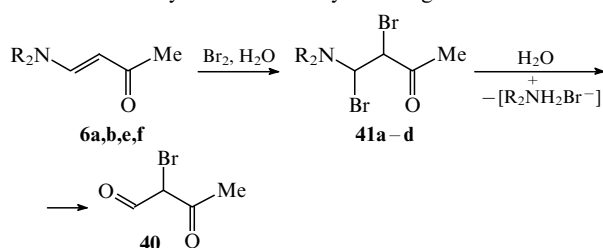
Evidence for primary hydration of the ethers **25a,b** was also obtained in kinetic studies of formation of 1,1-dialkyloxybutan-3-ones by GLC.^{111–113}

The reaction of 1-methoxypent-1-en-3-yne (**38a**), 1-methoxyhex-1-en-3-yne (**38b**) and 1-methoxyhept-1-en-3-yne (**38c**) with methanol and water under conditions of acid catalysis gave 1,1-dimethoxyalkan-3-ones **39a–c**, respectively.¹¹⁴



R = Me (a), Et (b), Prⁿ (c).

Derivatives of the aldehyde **36** containing functional groups in the methylene group have been synthesised. The synthesis of 2-bromo-3-oxobutanal (**40**) by direct bromination of the acetal **32** was described.¹¹⁵ However, reproduction of the experiments and structural analysis of the reaction products by GLC revealed the formation of three compounds, which suggests that bromination of the original acetal occurs in all the three possible directions.¹¹⁵ The bromosubstituted ketone **40** was synthesised in ~60% yield by bromination of enamino ketones **6a,b** in an aqueous medium. This reaction is accompanied by hydrolysis of 4-dialkylamino-3,4-dibromobutan-2-one **41** formed with elimination of the secondary amine and dehydrohalogenation.¹¹⁵

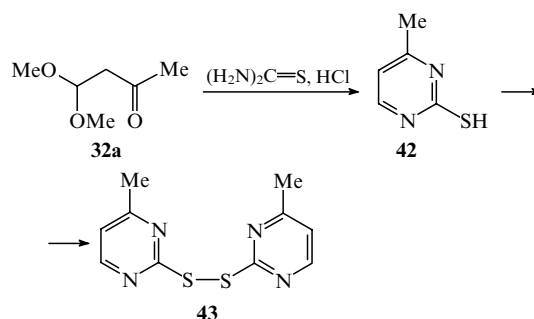


R = Me (**6a**, **41a**), Et (**6b**, **41b**); R₂N = (CH₂)₄N (**6e**, **41c**), (CH₂)₅N (**6f**, **41d**).

Intensive development of the chemistry of β -functionalised vinyl ketones has begun following synthesis of β -chlorovinyl methyl ketone by addition of acetyl chloride to acetylene.¹¹⁶ The synthetic potentialities of β -chlorovinyl ketones have been reviewed.^{116–118} The transfer of the acetylvinyl residue was named by A N Nesmeyanov and N K Kochetkov as 'ketovinylation'.¹¹⁹ The synthetic potential of this reaction was further expanded owing to the involvement of other β -substituted vinyl ketones RCOCH=CHY (Y = OR, NR₂, SR, NO₂, N₃,

SO₂R);¹²⁰ the activities and the selectivities of their reaction centres C(1) and C(3) can be altered by using different solvents.¹²¹

A pilot plant for the synthesis of the acetal **32b** based on dilute diacetylene-containing industrial gases accompanying manufacture of acetylene by electrocracking of methane (see Scheme 3) was installed at the Scientific-and-Industrial Association 'Azot' (Saratov) in 1974. The ether **25b** was obtained as a by-product.^{37,122} This version of diacetylene utilisation was implemented on an industrial scale with DMF and *N*-methylpyrrolidone as selective solvents. A pilot-plant unit for isolation of diacetylene formed as a side product in the manufacture of acetylene by oxidative pyrolysis of methane and preabsorption with ammonium was installed at the Scientific-and-Industrial Association 'Azot' (Novomoskovsk) in 1980.^{36,43,44,123–127} The technological process^{36,123} involved isolation of diacetylene from the bottoms of an ammonium preabsorption unit followed by the synthesis of the ether **25a**. Its hydration and methoxylation in the presence of catalytic amounts of H₂SO₄ yield the acetal **32a**, which is further used in the synthesis of 4-methylpyrimidine-2-thiol (**42**) by the reaction with thiourea in the presence of HCl and its oxidation product, viz., bis(4-methylpyrimidin-2-yl) disulfide (**43**).^{36,123}



The pyrimidinethiol and disulfide thus prepared accelerate the vulcanisation of rubbers having a unique spectrum of action.^{127,128} Their addition to rubber mixtures increases the resistance of the compositions to prevulcanisation by 150%. The disulfide **43** is a novel accelerant having a retarded initial period of action. The use of such accelerants prevents early cross-linking in processing of rubbers.^{128–130} Pyrimidinethiol **42** was used in the preparation of antitumour drugs¹³¹ and novel nematocides.¹³² It is also used as a lustre-enhancing coating in the production of electrolytic copper foils.^{36,133} The addition of small (0.003–0.03 g litre⁻¹) concentrations of this compound to electrolytes for the production of copper foil increases its yield by 60% and improves its physico-mechanical properties. The use of pyrimidinethiol **42** in the production of photographic materials for thermal development is widely known.¹³⁴

Thus, the interest in the practical use of diacetylene is determined by industrial demands, on the one hand, and by broad potentialities of the syntheses on the basis of 1,3-bifunctional compounds, on the other hand. The latter are the nearest derivatives of diacetylene and offer promising approaches to the synthesis of various classes of organic compounds. The list of products which can be prepared from diacetylene is given below.

Compound	Price per kg /USD ^a
1,1-Dimethoxybutan-3-one	201.75
(<i>E</i>)-4-Methoxybut-3-en-2-one	1716
1,3,3-Trimethoxybutane	1600
4-Diethylaminobutan-2-one	1290
Thiophene	236
5-Methylisoxazole	660
3-Methylpyrazole	2566
4-Methylpyrimidine	5200
2-Amino-4-methylpyrimidine	2117.5
4-Methylpyrimidine-2-thiol hydrochloride	770

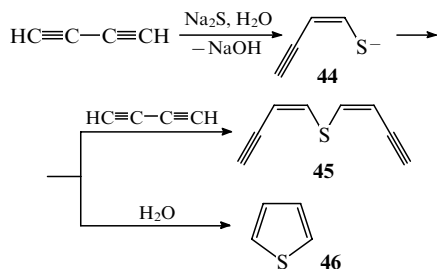
^aThe prices of 1997 are taken from Ref. 135.

V. Reactions with sulfur-containing nucleophiles

1. Reactions with hydrogen sulfide and sulfide ions

Systematic studies of reactions of acetylene and its derivatives with hydrogen sulfide and sulfide ions^{12, 17, 20, 23, 26–32, 136–138} have been extended to diacetylene.¹²

The reaction of diacetylene with hydrated sodium sulfide occurs through the formation of the ethynylvinylthiolate anion (**44**) and results in both di(2-ethynylvinyl) sulfide (**45**) and thiophene (**46**),^{12, 136–138} which is the product of cyclisation of the anion **44** or the corresponding thiol.



Earlier, an attempt was made¹³⁹ to synthesise thiophene from diacetylene by reaction of hydrated sodium sulfide with diacetylene in aqueous ethanol at pH 8–10; however, in this case the yield of the target product did not exceed 20%. When this reaction was carried out in a superbasic medium (KOH–DMSO), thiophene was obtained in high yields (up to 94%) and with high selectivity.^{12, 136} The sulfide **45** is not formed under these conditions. If the reaction is carried out in dimethyl sulfoxide, the addition of an alkali is unnecessary, since it is liberated in this reaction, but the yield of thiophene does not exceed 55%. The effect of reaction conditions on the yield of thiophene is demonstrated in Table 2.

Table 2. The effect of conditions of the reaction of diacetylene with sodium sulfide on the yield of thiophene (solvent, DMSO).

T /°C	Time /min	Concentration of reagents/mol		Yield of thiophene (%)
		C ₄ H ₂	Na ₂ S·9H ₂ O	
20	90	0.054	0.108	44.1
55	75	0.038 ^a	0.083	93.9
70	90	0.120	0.061	54.9
100	75	0.072	0.14	40.0

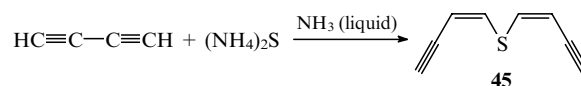
^a In the presence of 0.08 mol of KOH.

It should be emphasised that the addition of alkali is only necessary to trigger the synthesis, since the alkali liberated accelerates further the reaction. High selectivity of this reaction is worthy of note, *viz.*, the purity of raw thiophene distilled from the reaction mixture without additional purification reaches 99.9%.

Since this reaction represents nucleophilic addition of the sulfide ion to diacetylene with subsequent cyclisation of the intermediate product,¹⁴⁰ its rate should be higher in the solvents which do not suppress the activity of anions owing to their solvation. By virtue of their high dielectric permittivity, aprotic dipolar solvents (*e.g.*, DMSO, hexamethylphosphoric triamide) enhance electrolytic dissociation of sodium sulfide and sharply increase the concentration of the weakly solvated sulfide ion.¹⁴⁰ *N*-Methylpyrrolidone was also used as a solvent, and the reaction was carried out under identical conditions (55 °C, equimolar amounts of KOH and sodium sulfide). At 70 °C, the reaction of diacetylene with sodium sulfide carried out in an aqueous medium in the presence of an alkali gives thiophene in 52.5% yield.¹²

The conditions of the reaction of diacetylene with the sulfide ion giving exclusively the sulfide **45** (yields up to 89.5%) have been found.¹⁴⁰ In this reaction, liquid ammonia is used as a solvent and

sulfide ions are generated from ammonium sulfide formed *in situ* from ammonia and hydrogen sulfide:



The product **45** has *Z,Z*-configuration, which points to high *trans*-stereoselectivity of this reaction.¹⁴⁰

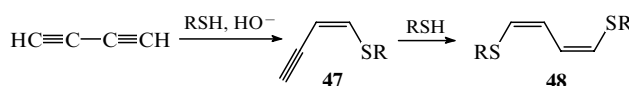
Among reactions of diacetylene with sulfur-containing compounds, synthesis of thiophene undoubtedly presents the greatest interest from the practical point of view. This stimulated the development of a procedure for continuous synthesis of thiophene from diacetylene and sodium sulfide in aqueous-alkaline media¹² with continuous removal of thiophene and replenishment of the reaction mixture with the starting reagents. Circulation of diacetylene lasted for 6 h at 70 °C; the yield of thiophene of 99% purity exceeded 70%. The results were reproducible. An increase in temperature caused a dramatic decrease in the yield of thiophene.

It should be noted that polymers formed from diacetylene in these media are not explosive. However, the synthesis performed in DMSO is more efficient, since it results in thiophene of high purity (99.9%) and in 94% yield.¹³⁶ The obvious advantages of this method include its simplicity, one-step procedure and wastelessness as well as high yields and high purity of the final product. Presumably, diacetylene present in waste gases from acetylene-manufacturing plants can also be used in large-scale productions, since the activities of the accompanying products (*e.g.*, methylacetylene, vinylacetylene) in the reaction with sulfide ions is much lower.¹²

2. Reactions with thiols

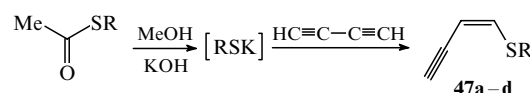
The addition of thiols to diacetylenes has been carried out under diverse conditions.³ In the presence of catalytic amounts of an alkali, thiols are easily added to one of the triple bonds of diacetylene to form 1-organylthio-1-en-3-yne **47**.³

This reaction is neither accelerated by free-radical initiators nor is decelerated by antioxidants, which suggests its heterolytic mechanism.³ Like many other ionic reactions of nucleophilic reagents with alkynes, it occurs as *trans*-addition and results in the *Z*-isomers **47**. However, this reaction is complicated by the addition of thiol to the sulfide **47** and the formation of 1,4-bis(organylthio)buta-1,3-dienes **48**, which significantly diminishes the yield of the primary adduct **47**.



R = Alk, Ar, Het.

The *in situ* generation of the thiolate anion from *S*-alkylisothiuronium salts¹⁴¹ or thioacetates¹⁴² under the action of alkalis prevents competitive free-radical addition of the free thiol thus reacting to sulfides **47** in high yields. The reaction of diacetylene with thioacetates is carried out in the presence of KOH (1.2 moles per mole of the starting acetate) with methanol as a solvent. This reaction gives sulfides **47** in up to 80% yields.^{141, 142}



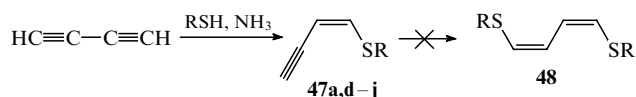
R = Et (**a**), Prⁿ (**b**), Prⁱ (**c**), Buⁿ (**d**).

The IR spectra of sulfides **47a–d** contain characteristic absorption bands at 3290 (≡CH), 2100 (C≡C) and 1560 cm^{–1} (C=C–S). In ¹H NMR spectra, the spin-spin coupling constant of vicinal protons (*J*_{HH}) is 10 Hz, *i.e.*, it is characteristic of the *cis*-arrangement of vinylic protons.

The use of liquid ammonia or of aqueous ammonia for nucleophilic thiolation of 1,3-diynes opens up new prospects for

the synthesis of unsaturated sulfides and practical utilisation of diacetylene in those technological processes where liquid ammonia is used as a selective solvent.³⁶

The reaction of diacetylene with thiols was studied¹⁴³ both in liquid ammonia and in aqueous ammonia at concentrations of ammonia varying from 25% to 70% within the temperature range of -33 to $+20$ °C. The aim of these studies was to reach the maximum use of the high solubilising capacity of ammonia with respect to diacetylene, which is determined by its moderate dielectric permittivity and polarity as well as by its relatively high basicity and ability to form hydrogen bonds and ammonium salts with thiols, which exist in ammoniacal solutions as contact ionic pairs and free ions. These factors altogether enhance the reactivity of thiolate ions, which are weakly solvated by ammonia. In fact, the reaction of diacetylene with thiols in liquid ammonia occurs under mild conditions (-33 °C) and is completed immediately after mixing of the reactants. Irrespective of the diacetylene: thiol molar ratio (1.0:0.5, 1:1, 1.0:1.2, 1:2), the selectivity of the reaction is not changed and the reaction results exclusively in sulfides **47** in 84% to 98% yields. This suggests that the secondary reaction leading to disulfides **48** is completely excluded in this case.¹⁴³



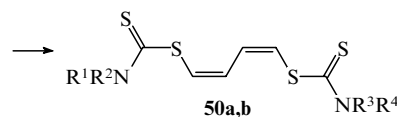
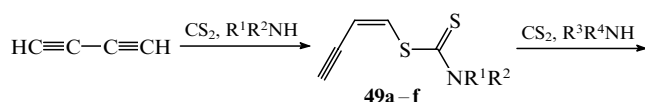
R = Et (**a**), Buⁿ (**d**), n-C₆H₁₃ (**e**), (CH₂)₂OH (**f**), CH₂CH(OH)CH₂OH (**g**), CH₂Si(OMe)₃ (**h**), (CH₂)₂Si(OMe)₃ (**i**), CH₂Si(OEt)₃ (**j**).

In this reaction, ammonia activates both the thiolate ion and diacetylene due to the formation of hydrogen bonds. The violation of the stereospecificity of the addition of thiols to diacetylene in liquid ammonia is attributed to the formation of diacetylene–ammonium complexes.¹⁴³ The adducts **47a,d–j** represent mixtures of *E*- and *Z*-isomers; the spin-spin coupling constants for the protons of *E*- and *Z*-ethylene fragments in the ¹H NMR spectra have characteristic values (15 and 10 Hz, respectively). The proportion of the *Z*-isomer increases with an increase in the bulk of the radical R, reaching a maximum (30%) in the case of compounds **47h–j**, *i.e.*, at the highest branching in the immediate vicinity of the sulfur atom. This suggests a significant contribution of spatial effects to the stereochemistry of this reaction, which seems to be predominantly kinetic, for the ratio of *E*- and *Z*-isomers is not changed after thermal treatment of the reaction products.

High reactivity of diacetylene with respect to thiols in liquid ammonia¹⁴³ permits, in principle, its quantitative isolation from gas mixtures in the form of sulfides **47**. Mild conditions of this reaction allow the involvement of thiols containing various functional groups.

3. The reaction with dithiocarbamate ions

Reactions of diacetylene with carbon disulfide and secondary amines or its direct reaction with ammonium dithiocarbamate in protic or aprotic solvents represent an efficient utilisation of diacetylene as a valuable product.¹⁴⁴ This reaction proceeds very easily in the absence of a catalyst when gaseous diacetylene is passed through a solution of a mixture of a secondary amine and carbon disulfide in MeOH, EtOH, Et₃N, THF, DMSO, acetone, benzene or ether or through a solution of dithiocarbamate at 20–50 °C and results in *s*-(*Z*)-(but-1-en-3-ynyl) *N,N*-dialkyldithiocarbamates **49** and 1,4-bis-(*N,N*-dialkylthiocarbamoylthio)-buta-1,3-dienes **50** in up to 94% yields.



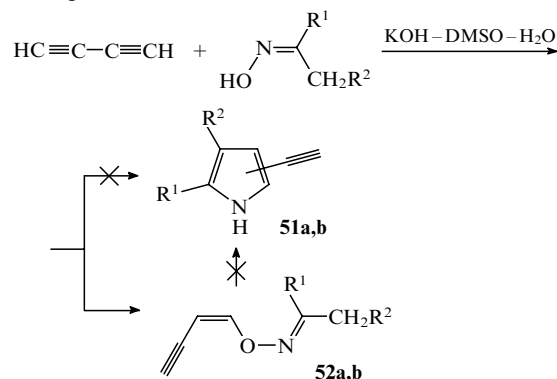
49: R¹ = R² = Et (**a**), Prⁿ (**b**); R¹–R² = (CH₂)₅ (**c**), (CH₂)₂O(CH₂)₂ (**d**); R¹ = R² = H (**e**), R¹ = H, R² = Me (**f**);

50: R¹ = R² = R³ = R⁴ = Et (**a**); R¹ = R² = Et, R³–R⁴ = (CH₂)₅ (**b**).

Mild conditions of this reaction are determined by high nucleophilicities of dithiocarbamate ions. The reaction products are *Z*-isomers.¹⁴⁴ However, the reaction of diacetylene with ammonium *N,N*-diethyldithiocarbamate is not stopped at the addition of one mole of dithiocarbamic acid and is complicated by further conversions resulting in the formation of bis(dithiocarbamate) **50**. Dithiocarbamates are used as nematocides and flotation agents^{145, 146} as well as in the production of photo-sensitive materials. The information about the use of alkynes in the synthesis of such esters is scarce.¹⁴⁷

VI. Reactions with ketoximes and amidoximes

It might be expected that the extension of the reaction of ketoximes with alkynes, which results in pyrroles (the Trofimov reaction),^{13, 15, 16, 22, 29, 90, 93} to diacetylene¹³ would open a route to the synthesis of ethynylpyrroles of the type **51** which could be regarded as promising monomers and reagents in fine organic synthesis. However, the route resulting in *O*-adducts, *e.g.*, *O*-(but-1-en-3-ynyl)ketoximes **52**, proved to be preferable due to the high reactivity of triple bonds of diacetylene with respect to nucleophilic reagents.^{13, 148, 149}

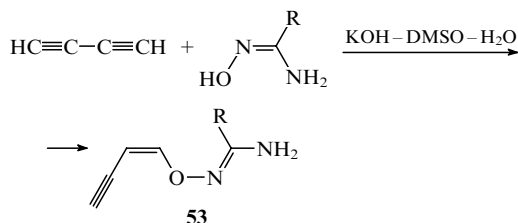


R¹ = Me, R² = H (**a**); R¹–R² = (CH₂)₄ (**b**).

In aqueous DMSO, diacetylene exothermally adds to ketoximes in the presence of catalytic amounts of alkalis resulting in vinylketoximes **52**.^{148, 149} It was of interest to find out whether more drastic conditions, which are normally used in the synthesis of pyrroles from ketoximes and acetylene, would result in cyclisation of vinylketoximes **52** through a [3,3]-sigmatropic shift characteristic of simple *O*-vinylketoximes.¹³ However, under different reaction conditions diacetylene reacted with ketoximes to give either vinylketoximes **52** or black-coloured insoluble polymers formed upon more profound transformations of diacetylene itself and its adducts.¹³ Ethynylpyrroles **51** were not found. The best yields of the adducts **52** (36%–41%) were obtained in the presence of ~10%–30% of water in DMSO and at a concentration of KOH 1%–2%. A decrease in the reagent's concentration increased the yield of the adduct, since polymerisation is inhibited under these conditions. An increase in the alkali concentration has a negative effect on the reaction yields. In neither case were bisadducts formed. The reaction of ketoximes with diacetylene is stereospecific and occurs as *trans*-addition. According to the ¹H NMR spectroscopic data, the adducts formed have *Z*-configuration (*J*_{HH} = 6.5–6.7 Hz), which corresponds to the nucleophilic addition to the triple bond with concerted attachment of a

proton from the reaction medium. Vinylketoximes **52** are rather unstable mobile fluids, these do not withstand heating up to 70–90 °C, being rapidly and quantitatively converted into a black insoluble powder even in solution. Thermolysis products largely contained polymers formed with involvement of the triple bonds. Pyrroles were not detected, either.

The reaction of diacetylene with amidoximes in the presence of KOH in aqueous DMSO gives *O*-adducts **53**. Their rearrangement into the corresponding ethynylimidazoles was not observed.¹⁵⁰

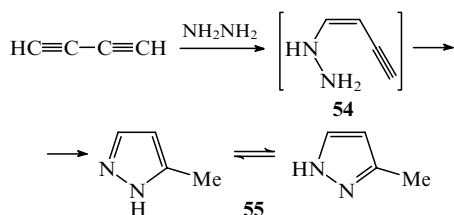


R = Me, Ph.

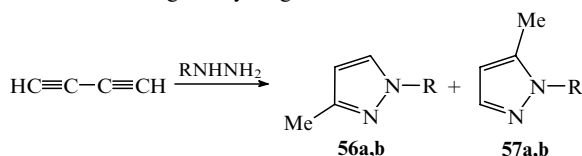
VII. Reactions with hydrazines and semicarbazide

In the syntheses of heterocyclic systems, 1,3- and 1,4-dicarbonyl compounds are widely used.¹⁵¹ The role of such C₃- and C₄-synthons can be played by 1,3-diyne.^{12, 13, 16, 17, 38–40}

Three independent groups of investigators reported simultaneously on the synthesis of pyrazole derivatives by addition of hydrazines to diacetylene and its mono- and disubstituted homologues.^{38, 39, 49, 56, 152–155} Apparently, hydrazine reacts with diacetylene as a primary amine to give an intermediate **54**; further intramolecular attack of the second amino group at the C(3) atom results in the formation of the pyrazole ring **55**.⁴⁸



Z-Configuration of the adduct favours the cyclisation. The condensation of methyl diacetylene with hydrazine hydrate gives 3,5-dimethylpyrazole together with 3(5)-ethylpyrazole,¹⁵⁵ which confirms the feasibility of another type of attack at the conjugated diyne system. In anhydrous media, the reactions of diacetylene with monosubstituted hydrazines result in 1,3-dialkylpyrazoles **56**, whereas 1,5-dialkylpyrazoles **57** are formed in the presence of water. The reaction of diacetylene with methylhydrazine in an ethanolic solution gives a mixture of pyrazoles **56a** and **57a** (4 : 1), which corresponds to the predominant attack of hydrazine at the carbon atom bearing the hydrogen atom.¹⁵⁶



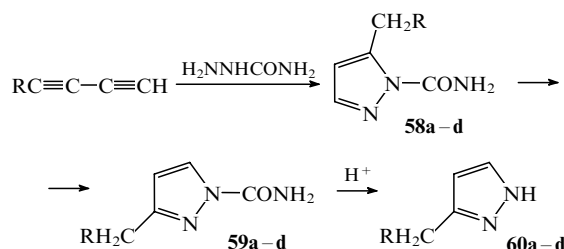
R = Me (a), Et (b).

Pyrazole **55** has become accessible due to the reaction of diacetylene with hydrazine.^{152, 154, 155} Direct synthesis of pyrazoles seems to be one of possible clues to the practical solution of the problem of diacetylene utilisation;¹⁵⁵ the resulting pyrazoles with various substituents are used as starting compounds in the synthesis of *C*- and *N*-vinylpyrazoles.¹⁵⁵

Syntheses of vinylpyrazoles and their homo- and copolymerisation acquired further development.^{157–159} Syntheses of biological additives to polymeric materials based on pyrazoles

prepared from diacetylene were also described.^{157, 158} The synthesis of *C*-vinylpyrazoles from pyrazole **55** was carried out.¹⁵⁹ Vinyl derivatives of some azoles, including pyrazole, were used in various branches of industry, such as production of plastics and synthetic fibres, radio engineering and medicine.¹⁵⁹ Some novel herbicides,^{160–162} pesticides,^{163, 164} antidiabetic drugs,¹⁶⁵ immunostimulators¹⁶⁶ and perfume compositions¹⁶⁷ prepared from pyrazoles **55–57** have been covered by patents. Synthesis of polychelating agents of the pyrazole series designed for solidification of epoxide resins was described.¹⁵⁷ The possibilities of extractive isolation of noble metals (Pd, Au, Ag) with pyrazole **55** hydrochlorides,^{168, 169} of preparation of complex-forming ion-exchange resins,^{170, 171} absorbents for concentration of platinum metals,¹⁷² nitration catalysts¹⁷³ and disproportionation catalysts in the synthesis of monoalkyl- and monoaryl-halogenosilanes¹⁷⁴ were demonstrated.

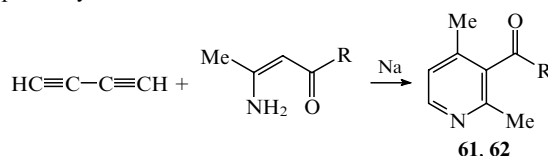
The reaction of diacetylene with semicarbazide, which manifests much weaker basic properties than hydrazines, yields a mixture of 3- and 5-alkylpyrazolecarboxamides (**58**, **59**).¹⁷⁵ The amides **58**, which are irreversibly isomerised into the adducts **59** under these conditions, are the main reaction products.¹⁷⁵ Other 1,3-diyne produce exclusively amides of the type **59**.¹⁷⁵



R = H (a), Me (b), Et (c), Prⁿ (d).

The presence of a pyrazole ring was confirmed¹⁷⁵ by acid hydrolysis of the adducts **59**, which was accompanied by decarboxylation and formation of pyrazoles **60**. Synthesis of 1-guanyl-3-methylpyrazole (yield 86%) from pyrazole **55** was described.¹⁷⁶ Pyrazole-1-carboxylic acid derivatives are used as pesticides¹⁷⁷ and insecticides.¹⁷⁸

Functionalised pyridines were prepared based on diacetylene and compounds containing a weakly nucleophilic nitrogen atom and an active CH-component (*e.g.*, acetylacetoneimine and ethyl β-aminocrotonate).^{176–178} The reaction products are 3-acetyl-2,4-dimethylpyridine (**61**) and ethyl 2,4-dimethylnicotinate (**62**), respectively.



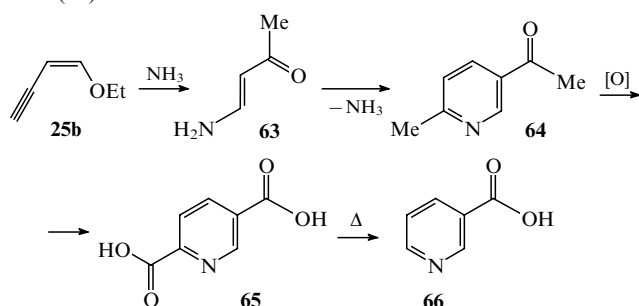
R = Me (**61**), OEt (**62**).

Since the nucleophilicity of the nitrogen atom in the starting enamino ester and the enamino ketone is lowered, the reaction with diacetylene occurs in the presence of metallic sodium.

The formation of one of two possible isomers in both reactions was confirmed by ¹H NMR and IR spectroscopy as well as by chromatography. Moreover, pyridine **62** was obtained independently by oxidation of ethyl 2,4-dimethyl-1,4-dihydropyridine-3-carboxylate synthesised from crotonaldehyde and ethyl β-aminocrotonate.¹⁷⁸ The IR spectra of compounds **61** and **62** contain bands corresponding to stretching vibrations of the pyridine ring (1560, 1580 cm^{−1}), ester (1076 cm^{−1}) and carbonyl (1721 cm^{−1}) groups.^{176, 178} The protons of the pyridine ring in the ¹H NMR spectrum of compound **62** resonate as two doublets in the low-field region at δ 8.24 and 6.84 (*J* = 5.2 Hz). The former belongs to the proton at the C(6) atom, which is especially strongly

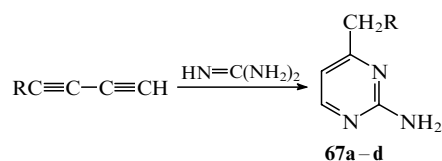
desielded by the nitrogen atom of the pyridine ring, while the latter corresponds to the proton at the C(5) atom.

Pyridines prepared from diacetylene are candidates for the synthesis of nicotinic acid. However, the above-described reaction is inefficient because of low yields of the target products. A promising procedure for large-scale synthesis of nicotinic acid was developed^{37, 130} on the basis of 4-aminobut-3-en-2-one (**63**) obtained by transamination of the ether **25b**.⁵⁸ Aminobutenone **63** cyclises spontaneously into 5-acetyl-2-methylpyridine (**64**),¹⁷⁹ which is further oxidised to pyridine-2,5-dicarboxylic (isocinchomeric) acid (**65**), which in turn is decarboxylated into nicotinic acid (**66**) at 200 °C.³⁷



VIII. Reactions with guanidine

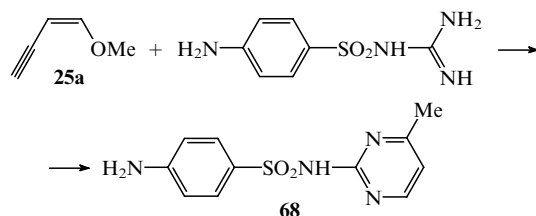
The reaction of diacetylene and monosubstituted 1,3-diynes with guanidine in the presence of equimolar amounts of metallic sodium yields 4-alkyl-2-aminopyrimidines **67**.^{180, 181}



$\text{R} = \text{H}$ (**a**), Me (**b**), Et (**c**), Pr^n (**d**).

The structure of cyclisation products was established by a comparison of physical constants of isolated compounds and their picrates with those of known compounds obtained by independent synthesis.^{180, 181}

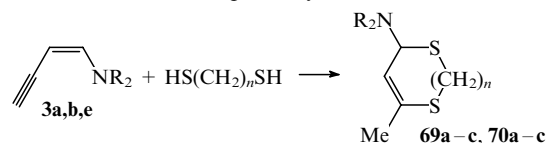
Amines of the pyrimidine series are widely used in large-scale organic synthesis, particularly, in the pharmaceutical industry.¹⁸² Some of them are intermediates in the synthesis of sulfonylamide drugs, e.g. sulfamerazine 2-(*p*-aminophenylsulfonylamido)-4-methylpyrimidine (**68**),¹⁸² which can be prepared in high yields from the acetal **32a** or the ether **25a**.¹³⁰



Sulfamerazine (**68**) is less toxic and more easily accessible (one-step procedure, high yields) than the well-known drug sulfodimezine [2-(*p*-aminophenylsulfonylamido)-4,6-dimethylpyrimidine] prepared from 2-amino-4,6-dimethylpyrimidine by a six-step procedure. Sulfamerazine is manufactured by the pharmaceutical company 'Polfa' and is used in the treatment of streptococcal and pneumococcal infections. Some derivatives of the pyrimidine **67a**, which include protein tyrosine kinase inhibitors,¹⁸³ vitronectin receptor antagonists,¹⁸⁴ potent psychotropic drugs,¹⁸⁵ novel fungicides¹⁸⁶ and perfume compositions,^{187, 188} were patented.

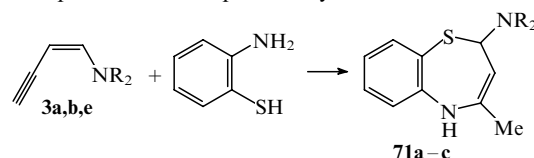
IX. 1-Dialkylaminobut-1-en-3-yne as building blocks for the synthesis of heterocyclic compounds

Some cyclisation reactions occur exclusively with the amines **3**. Their reaction with 1,2-ethanedithiol and 1,3-propanedithiol result in 5-dialkylamino-7-methyl-5*H*-2,3-dihydro-1,4-dithiopynes **69a-c** and 2-dialkylamino-4-methyl-2,6,7,8-tetrahydro-1,5-dithiocines **70a-c**, respectively.^{189, 190}



$\text{R} = \text{Me}$ (**3a**, **69a**, **70a**), Et (**3b**, **69b**, **70b**); $\text{R}_2\text{N} = \text{N}(\text{CH}_2)_2\text{O}$ (**3e**, **69c**, **70c**); $n = 2$ (**69a-c**), 3 (**70a-c**).

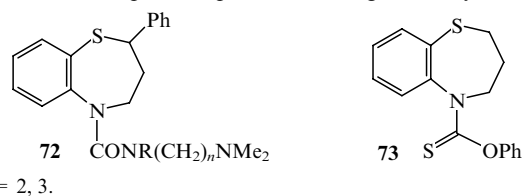
The condensation of 2-aminobenzenethiol with the amines **3a,b,e** is performed at room temperature in the absence of a catalyst and gives 2-dialkylamino-4-methyl-2,5-dihydro-1,5-benzothiazepines **71a-c** in up to 90% yields.^{190, 191}



$\text{R} = \text{Me}$ (**3a**, **71a**), Et (**3b**, **71b**); $\text{R}_2\text{N} = \text{N}(\text{CH}_2)_2\text{O}$ (**3e**, **71c**).

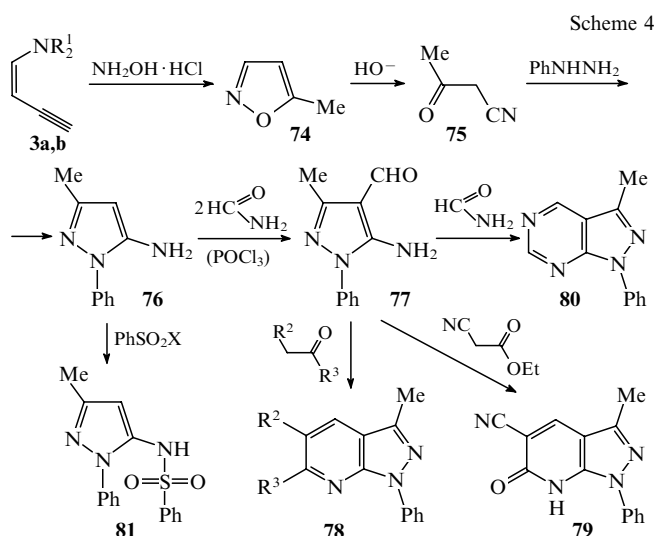
High yields of the reaction products and the absence of routes to their direct synthesis from diacetylene makes this method for the preparation of thiazepines promising.

1,4-Dithiopyne derivatives are biologically active and can be used as tranquillisers.^{192, 193} 1,5-Benzothiazepines manifest antiarrhythmic activity¹⁹⁴ and are used as regulators of the cardiovascular function.^{195, 196} Compounds **72** are tranquillisers,¹⁹⁷ and 1,5-benzothiazepines **73** possess antifungal activity.¹⁹⁸



The salient advantage of 1-dialkylaminobut-1-en-3-yne over diacetylene and its other derivatives as building blocks becomes especially obvious in the synthesis of isoxazoles. The latter cannot be obtained by the reaction of diacetylene with hydroxylamine hydrochloride.⁴⁷ 1-Alkoxy- and 1-alkylthiobutenynes give a mixture of 3- and 5-methylisoxazoles.^{37, 38, 47} On the other hand, 1-dialkylaminobut-1-en-3-yne **3** give exclusively 5-methylisoxazole (**74**) in reaction with hydroxylamine (Scheme 4).^{37, 47} The latter yields cyanoacetone (**75**) upon alkaline treatment.¹⁹⁹ Cyanoacetone reacts with phenylhydrazine to give the cyclisation product, viz., 5-amino-3-methyl-1-phenylpyrazole (**76**).³⁷ The latter is subjected to Wilsmeier-Haack formylation to give 5-amino-3-methyl-1-phenylpyrazole-4-carbaldehyde (**77**),²⁰⁰ which is used in the construction of fused pyrazolopyridines **78** and **79** and pyrazolopyrimidines **80** (see Scheme 4).^{201, 202}

Novel long-acting sulfonylamide drugs of the type **81** can be prepared from the isoxazole **74**.²⁰² Aminopyrazole **76** is used in the synthesis of pharmacologically active compounds (e.g., antidepressants, anticonvulsants, analgesics, etc.),²⁰³ biologically active reagents, some key synthons,²⁰⁴ diazo dyes for colour offset,²⁰⁵ heterocyclic anionic monoazo dyes²⁰⁶ and compositions for colour photography.²⁰⁷⁻²⁰⁹

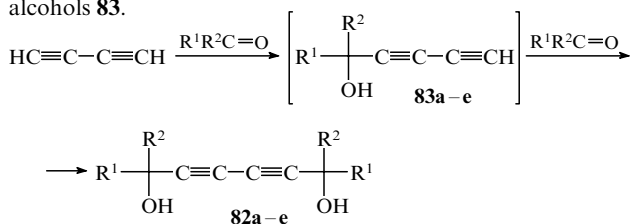


$R^2 = R^3 = \text{Me, Et.}$

X. Reactions with carbonyl compounds

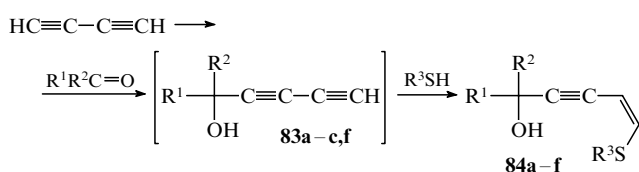
General methods for the synthesis of diacetylene alcohols and glycols include the reaction of sodium derivatives of 1,3-diynes with carbonyl compounds in liquid ammonia, condensation of mono- and bis(bromomagnesium) derivatives of 1,3-diynes with aldehydes and ketones in THF, the Favorsky condensation of 1,3-diynes with carbonyl compounds in the presence of KOH powder in ether or THF, oxidative condensation of α -acetylenic alcohols in the presence of copper salts and the Hodkevich–Kadyo condensation of monoacetylenic alcohols.³

This review provides a detailed description of reactions of diacetylene with carbonyl compounds which are applicable to industrial diacetylene and result in the formation of valuable products. Since some technological schemes used in acetylene production include selective extraction of diacetylene with liquid ammonia,³⁶ its extraction with ammoniacal and aqueous ammoniacal solutions also seems to be efficient. A one-step procedure was developed for the synthesis of bis-tertiary diacetylenic glycols by the reaction of diacetylene with ketones in the presence of a catalytic system (ammonia–water–alkali).²¹⁰ The use of a small excess of the ketone allows preparation of glycols **82** in nearly quantitative yields without the formation of the diacetylenic alcohols **83**.



82, 83: $R^1 = R^2 = \text{Me}$ (**a**); $R^1 = \text{Me}$, $R^2 = \text{Et}$ (**b**); $R^1-R^2 = (\text{CH}_2)_5$ (**c**); $R^1 = \text{Me}$, $R^2 = \text{Bu}^n$ (**d**); $R^1 = \text{Me}$, $R^2 = n\text{-C}_6\text{H}_{13}$ (**e**).

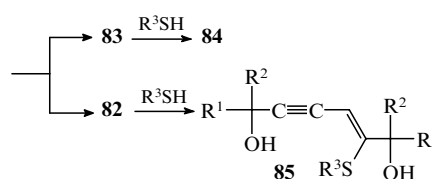
A simple and efficient one-pot synthesis of tertiary alkylthioenynol alcohols **84** from diacetylene, ketones and thiols in liquid ammonia has been developed.^{211–214}



Diacetylenic alcohols 83	R^3 in the thiol $R^3\text{SH}$	Thioalcohol 84
83a ($R^1 = R^2 = \text{Me}$)	Et	84a
	Pr^n	84b
	Bu^n	84c
83b ($R^1 = \text{Me}$, $R^2 = \text{Et}$)	Et	84d
83c ($R^1-R^2 = (\text{CH}_2)_5$)	Et	84e
83f ($R^1-R^2 = (\text{CH}_2)_4$)	Et	84f

The alcohols **84a–f** are characterised by a broad spectrum of biological activities and exhibit interest as monomers and intermediates for fine organic synthesis and for the pharmaceutical industry.²¹⁵

Condensation of diacetylene with ketones in the presence of catalytic amounts of an alkali (0.01–0.1 moles per mole of $\text{HC}\equiv\text{C}-\text{C}\equiv\text{CH}$) in liquid ammonia with subsequent addition of a thiol was studied with the aim of developing a reliable procedure for the synthesis of alkylthioenynol alcohols **84** and glycols **85**.²¹³ This reaction is carried out with a 6%–10% diacetylene solution in liquid NH_3 at the temperature of liquid ammonia and at the diacetylene:ketone:thiol molar ratio of 1.0:0.5:1.2. Alkali metal cations catalyse the condensation of diacetylene with ketones and simultaneously accelerate the reaction of diacetylenic alcohols **82** with thiols resulting in compounds **84** (yields 83%–96%).²¹³ An excess of diacetylene (relative to the ketone) directs the reaction towards the formation of diacetylenic alcohols. Alkylthioenynol glycols **85** are formed in 89% to 95% yields at the diacetylene:ketone:thiol molar ratio of 1.0:2.0:1.3.^{213, 216}

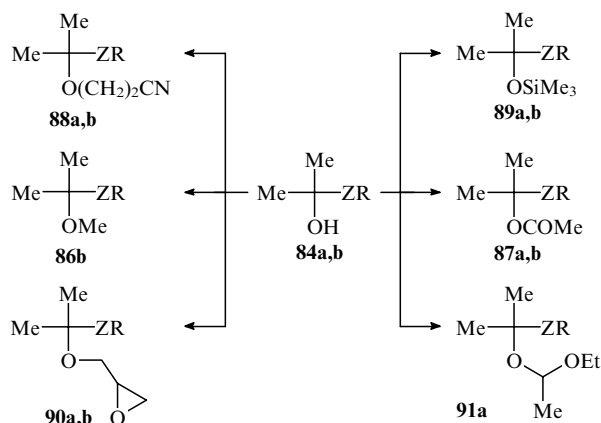


$R^1 = \text{Me}$; $R^2 = \text{Me, Et}$; $R^1-R^2 = (\text{CH}_2)_4$;

$R^3 = \text{Et, Pr}^n, \text{Pr}^i, \text{Bu}^n, \text{Bu}^i$.

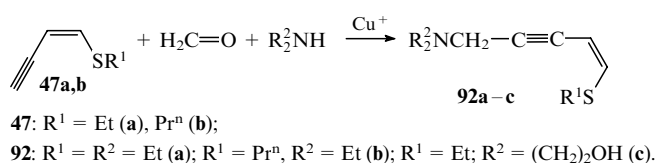
The sulfides **84** can also be synthesised by the condensation of enynyl sulfides **47** with acetone under conditions of the Favorsky reaction.²¹⁷ Since the presence of the hydroxy functional group often excludes the possibility of selective attack at other reaction centres, Volkova *et al.*²¹¹ have converted alcohols **84a,b** into ethers (**86b**), esters (**87a,b**), β -cyanoethyl (**88a,b**), trimethylsilyl (**89a,b**) and glycidyl (**90a,b**) derivatives and acetals (**91a**) (Scheme 5).

Scheme 5



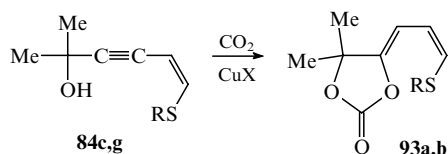
$\text{ZR} = \text{C}\equiv\text{C}-\text{CH}=\text{CH}-\text{SR}$, where $R = \text{Et}$ (**a**), Pr^n (**b**).

The functionalisation of the thioethers **47a–c** was described.¹⁴² These sulfides, contrary to the published data,³ enter into the Mannich reaction with secondary amines on heating in dioxane in the presence of copper(I) chloride to give 1-alkylthio-5-dialkylaminopent-1-en-3-yne **92a–c**.



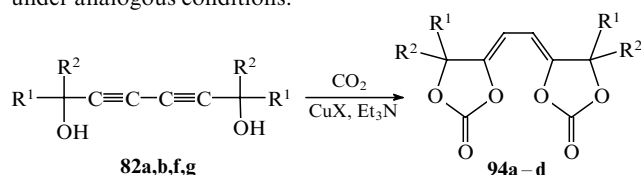
The reaction of 2-methyl-6-phenylhexa-3,5-diyn-2-ol with alcohols and ketones²¹⁸ was used to obtain the corresponding ethynylvinyl ethers and dioxolanes which contain an enyne fragment in the side chain and manifest pharmacological activities.²¹⁹

An unusual reaction of tertiary alkylthioenynol alcohols **84** with CO₂ was carried out under a pressure of 70–73 atm at 70–75 °C in the presence of catalytic amounts of copper(I) salts and triethylamine without solvents.^{220, 221} The products of this reaction are 5-(3-alkylthioprop-2-enylidene)-4,4-dimethyl-1,3-dioxolan-2-ones **93a,b**.²²⁰



R = Buⁿ (**84c**, **93a**), Me (**84g**, **93b**); X = Cl, OAc.

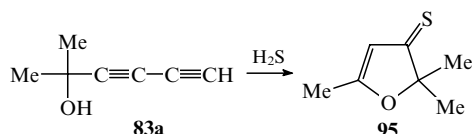
Stable 1,2-bis(1,3-dioxolan-2-on-5-ylidene)ethanes **94a–d** are formed from diacetylenic glycols **82a–d** in more than 90% yields under analogous conditions.²²¹



X = Cl, OAc.

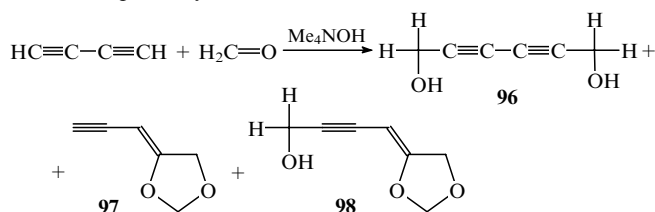
R ¹	R ²	Glycol 82	Product 94
Me	Me	82a	94a
Me	Et	82b	94b
Pr ⁿ	Pr ⁿ	82f	94c
(CH ₂) ₄		82g	94d

The reaction of the tertiary diacetylenic alcohol **83a** or the bis-tertiary diacetylenic glycol **82a** with hydrogen sulfide²²² in the presence of alkaline catalysts result in dihydrofuranthione **95**.

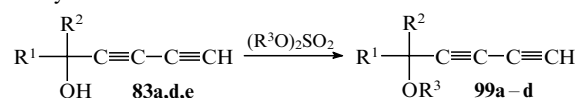


Condensation of diacetylene with carbonyl compounds was carried out under conditions close to the industrial ones.^{223–225} 2,7-Dimethylocta-3,5-diyne-2,7-diol (**82a**) was obtained in 72% yield (acetone, 25% aqueous NH₃, 0.01–0.04 mole of KOH or NaOH per mole of acetone, 10-fold excess of diacetylene).²²⁴ A decrease in the catalyst's concentration to 0.01 mole decreases the yield of glycol to 11% and simultaneously increases the yield of 2-methylhexa-3,5-diyn-2-ol (**83a**) from 9% to 61%. An increase in the ammonia concentration in the reaction mixture directs the reaction exclusively towards the formation of glycol **82a**; its yield reaches 94%. Butylmethyl- and hexylmethyl ketones react with diacetylene in the presence of an alkali (0.3 mole per mole of ketone) to form diacetylenic alcohols **83** (yields ~ 60%).²²⁴ It was

shown that the anion-exchange resin AB-17-8P(OH) catalyses the condensation of diacetylene with carbonyl compounds.²²⁶ Tetramethylammonium hydroxide also catalyses the reaction of diacetylene with formaldehyde.²²⁷ The reaction with formaldehyde occurs smoothly at 20–40 °C and yields, in addition to hexa-2,4-diyne-1,6-diol (**96**), 1,3-dioxolanes **97** and **98** which are the products of subsequent reaction of formaldehyde with the diol **96** and 2,4-pentadiynol.²²⁷

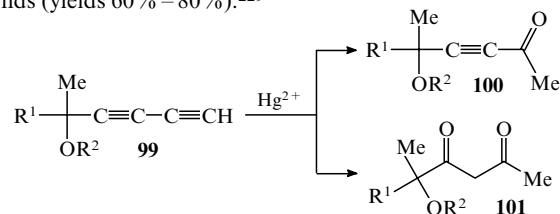


Alkylation of alcohols **83a–d** (dialkyl sulfate, 5–15 °C, 2 h) was used to prepare ethers of tertiary diacetylenic alcohols **99** in up to 80% yields.²²⁸



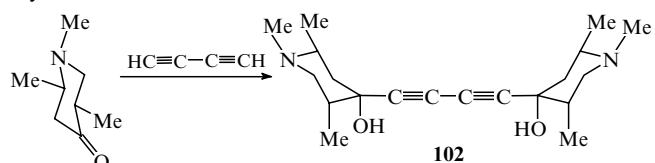
R ¹	R ²	R ³	Alcohol 83	Ether 99
Me	Me	Me	83a	99a
Me	Me	Bu ⁿ	83a	99b
Me	n-C ₆ H ₁₃	Me	83e	99c
Me	Bu ⁿ	Et	83d	99d

β-Diketones and acetylenic ketones were synthesised from ethers **99**.²²⁹ In the presence of HgSO₄ (1 h, 65–70 °C), the hydration of the terminal triple bond of the ethers **99** gives ketones **100** in up to 93% yields.²²⁹ β-Diketones **101** are formed with an increase in temperature to 80 °C and with larger amounts of HgSO₄ in 8–10 h as a result of total hydration of both triple bonds (yields 60%–80%).²²⁹



A number of papers are devoted^{230–237} to the synthesis of potentially physiologically active compounds based on acetylenic and diacetylenic alcohols and glycols as well as to the analysis of biological activities of reaction products and their applications in agriculture.

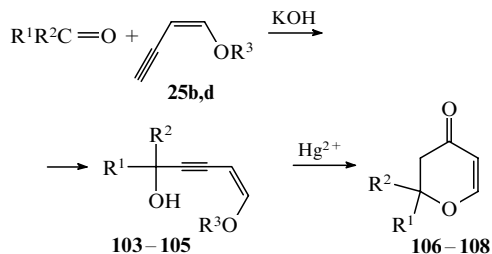
It was shown that diacetylene and diynes containing terminal triple bonds add to the carbonyl group of 1,2,3-trimethylpiperidin-4-one under conditions of the Favorsky reaction to yield a mixture of isomeric alcohols and glycols containing predominantly epimers **102**, the products of axial addition of diynes to the C=O bond.^{230–237}



A correlation was found between the biological activity and chirality of asymmetrical diacetylenic glycols.²³⁰ Acpinol, which represents a product of exhaustive hydrochlorination of a mixture of isomers of the glycol **102**, was recommended for use in agriculture.^{236–240} A method of manufacture of acpinol employs diacetylene present in the abgases from acetylene-manufacturing

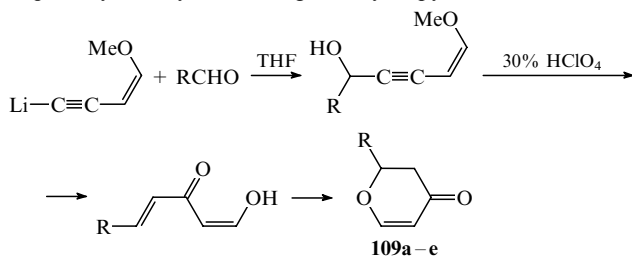
plants. The purity of the product depends on the composition of the abgas.²³⁰

The cyclohydration of alkoxyvinylacetylenic alcohols **103–105** obtained from ethoxybutenyne (**25b**) and butoxybutenyne (**25d**)^{241, 242} under conditions of the Kucherov reaction or in dilute H₂SO₄ at room temperature results in dihydropyran-4-ones **106–108**.^{243, 244}



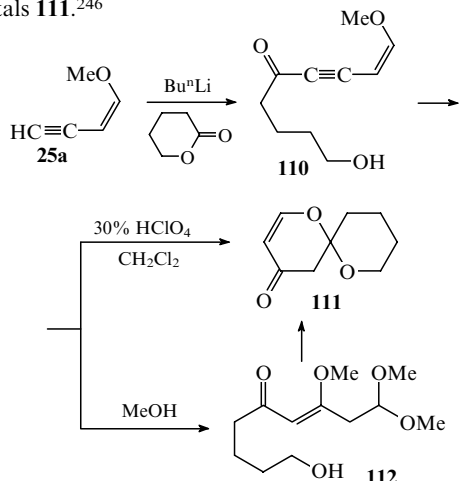
R¹ = R² = Me (**103**, **106**); R¹–R² = (CH₂)₅ (**104**, **107**);
R¹–R² = (CH₂)₂NMe(CH₂)₂ (**105**, **108**); R³ = Et (**b**), Buⁿ (**d**).

The synthesis of 2-alkyl-2,3-dihydro-γ-pyrones **109** from the ether **25a** and aldehydes was described.²⁴⁵ Condensation of lithium methoxybutenyne with various aldehydes (from MeCHO to iso-C₅H₁₁CHO) in THF at –78 °C yields secondary alcohols which undergo hydration at the triple bond with subsequent cyclodehydration to give dihydropyrones **109a–e**.²⁴⁵



R = Me (**a**), Et (**b**), Prⁿ (**c**), Prⁱ (**d**), iso-C₅H₁₁ (**e**).

The yield of the reaction products increases with an increase in the length of the alkyl radical. Thus pyrones **109a** and **109e** are formed in 40% and 80% yields, respectively. The reaction of the lithium derivative of the ether **25a** with lactones affords spiroketals **111**.²⁴⁶



For example, the hydroxy ketone **110** was obtained from δ-valerolactone in THF at –78 °C in 98% yield. Its conversion into the spiroketal **111** can be carried out in two ways,²⁴⁶ viz., by direct conversion under the action of 30% HClO₄ in CH₂Cl₂ (yield 58%) or *via* an intermediate trimethoxy ketone **112** (yield 86%). These dihydropyrones are used as fungicides.²⁴⁷

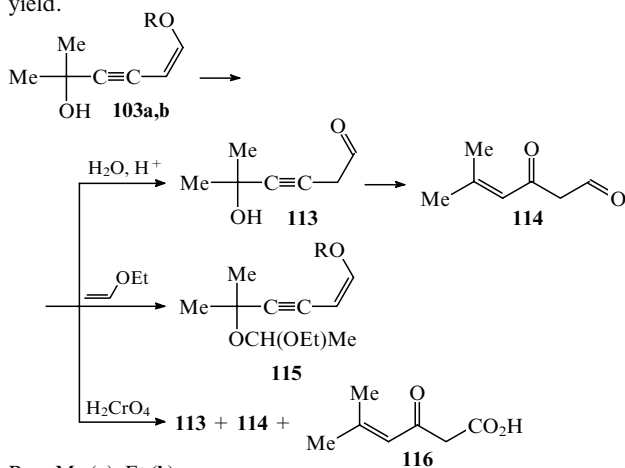
A general method for the synthesis of functionalised spiroketals from lactones and (Z)-lithium derivatives of the ether **25a** was proposed.²⁴⁸

Some novel antiinflammatory drugs and a pharmaceutically stable inhibitor of LTA₄-hydrolase based on the *E*-isomer of the ether **25a** were patented.²⁴⁹ These compounds are used as constituents of composite fuels for stabilisation of combustible mixtures.²⁵⁰

Ethynylation with diacetylene was used in the synthesis of additives to perfume compositions, *e.g.*, 2,6,11,15-tetramethylhexadecane-6,11-diol²⁵¹ or 6,11-dihydroxycroctane and croctane.²⁵² A commercial synthesis of squalane by ethynylation of geranylacetone with a diacetylene–*N*-methylpyrrolidone complex (1:1) in the presence of KOH with subsequent reduction over Raney nickel was described.²⁵³

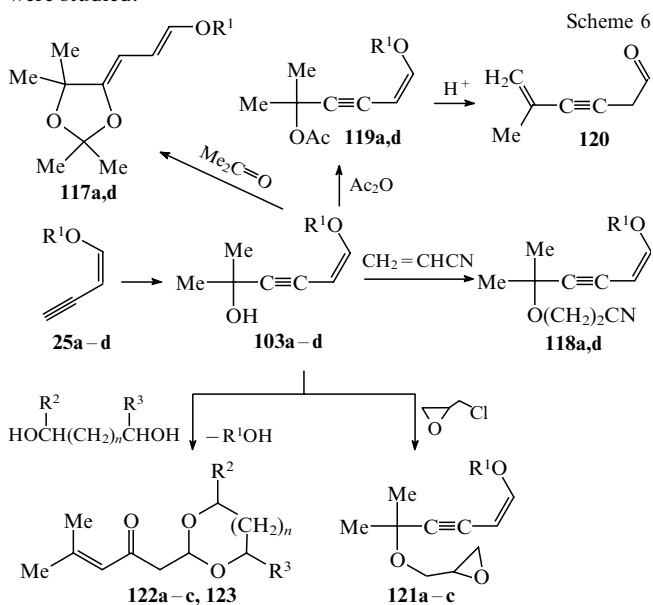
The alkoxy- and alkylthioenynes alcohols prepared from diacetylene can be used in the synthesis of various polyfunctional unsaturated compounds.²⁵⁴

Hydrolytic scission of vinyl ethers **103a,b** by dilute acids results in acetylenic hydroxy aldehydes **113**, which are readily isomerised into oxoaldehydes **114** in up to 75% yields.²⁵⁴ The reaction of vinyl ethers **103a,b** with ethyl vinyl ether was used to obtain acetals **115** (yield 80%). The oxidation of vinyl ethers **103a,b** with chromic acid in acetone gives a mixture of aldehydes **113** and **114** in a total yield of 61% and the oxo acid **116** in 10% yield.



R = Me (**a**), Et (**b**).

Reactions of tertiary alcohols **103a–d** with acetone, acrylonitrile, acetic anhydride, epichlorohydrin and glycols (Scheme 6) were studied.²⁵⁵



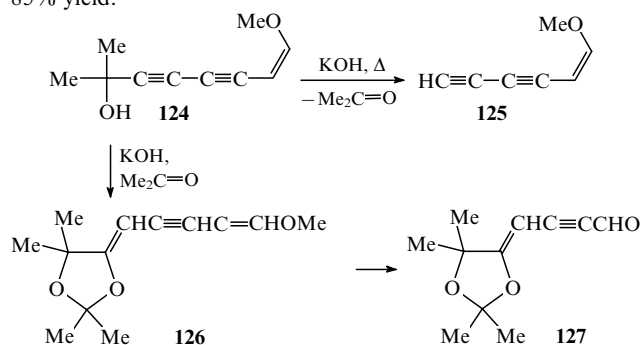
R¹ = Me (**a**), Et (**b**), Prⁿ (**c**), Buⁿ (**d**);
R², R³ = H, Me; *n* = 0 (**122**), 1 (**123**).

The reactions of the vinyl ether **103a,d** with acetone result in 5-(3-alkoxyallylidene)-2,2,4,4-tetramethyl-1,3-dioxolanes **117a,d**.²⁵⁵ Cyanoethylation of these ethers with acrylonitrile occurs in the presence of an 40% aqueous solution of KOH or MeONa in *tert*-butyl alcohol and results in 1-alkoxy-5-(2-cyanoethoxy)-5-methylhex-1-en-3-yne **118a,d** in up to 50% yields. Acetylation of the alcohols **103a,d** with acetic anhydride in pyridine at 70–90 °C results in 5-acetoxy-1-alkoxy-5-methylhex-1-en-3-yne (**119a,d**) in 21% to 49% yields.²⁵⁵ During distillation, acetates undergo deacetylation and dehydration to give the enynal **120**.²⁵⁵ The reaction of epichlorohydrin with ethers **103a–c** in an alkaline medium afforded glycidyl ethers **121a–c** in 60%–65% yields (see Scheme 6).²⁵⁶ The resulting products are candidates for epoxy-containing monomers.²¹⁵

The reaction of bisprimary and primary-secondary α - and β -glycols with ethers **103a,b,d** in the presence of the Newland catalyst ($\text{HgO} - \text{BF}_3$) results in 2-(4-methyl-2-oxopent-3-enyl)-1,3-dioxolanes **122** in up to 64% yields (see Scheme 6).²⁵⁷ Presumably, this reaction begins with isomerisation of the alkoxy-enyne alcohol into an unstable alkoxydivinyl ketone. The latter adds a glycol molecule to give an asymmetrical hydroxy acetal, which easily loses the alcohol molecule and cyclises into 1,3-dioxolanes **122** or 1,3-dioxanes **123**.²⁵⁷ Moderate neuroactivity of 1,3-dioxolanes and 1,3-dioxanes prepared on the basis of alkoxy-enyne tertiary alcohols was established.²⁵⁸

It is worth noting that the most reactive compounds of this series manifest both general depressant activity and a stimulating effect on the central adreno- and dopaminergic systems of the brain, which makes them similar to antidepressants.²⁵⁸

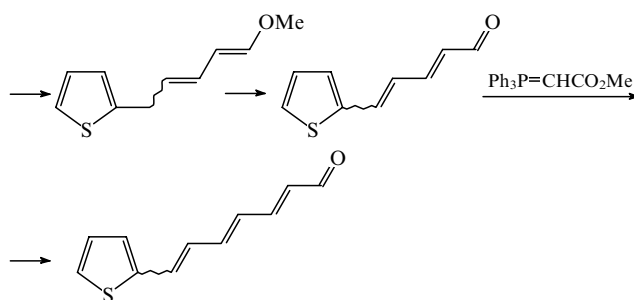
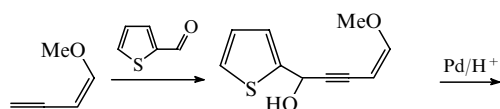
Base-catalysed thermolysis (the retro-Favorsky reaction) of 8-methoxyoct-7-ene-3,5-diyn-2-ol (**124**) was studied.²⁵⁹ In organic media, this is accompanied by different reactions the direction of which depends on the nature of the solvent.²⁵⁹ In benzene or THF, the thermolysis at the boiling temperature of the reaction mixture results in the formation of 1-methoxyhex-1-ene-3,5-diyne (**125**) in 85% yield.²⁵⁹



The formation of 2,2,4,4-tetramethyl-5-(5-methoxypent-4-en-2-ynylidene)-1,3-dioxolane (**126**) isolated from the reaction mixture as a side product can be attributed to the reaction of the original alcohol with acetone in the presence of KOH. In air, the product **126** is oxidised to 2,2,4,4-tetramethyl-5-(3-formylpropynylidene)-1,3-dioxolane (**127**).²⁵⁹

Vinyl ethers **103** react with nitrogen bases (hydrazine, methylhydrazine, hydroxylamine) in acid and alkaline media with the formation of heterocyclic compounds of the pyrazole and isoxazole series.²⁶⁰

Some natural thiophene derivatives (*e.g.*, 7-thienylheptatrienal) were synthesised from (*E*)-methoxybutenyne and thiophene-2-carbaldehyde.²⁶¹



XI. Conclusion

The data accumulated thus far demonstrate the possibility of utilisation of diacetylene in industrial syntheses of valuable products, reagents, starting compounds for pharmaceutical industry, materials for new technologies, *etc.*

The processes aimed at acetylene production based on pyrolysis of hydrocarbon raw materials will long be used as a source for large-tonnage synthesis of diacetylene the utilisation of which is still a challenge for chemists and also common sense, since combustion of hydrocarbon gases is most senseless in this case. As D I Mendelev used to say, 'one can fire a furnace with banknotes'.²⁶²

It has now become quite clear that diacetylene can be used for small-capacity, profitable manufacture of thiophene, vitamins A and PP, geraniol and phytol derivatives, pyrazoles, pyrimidines and pyridines. Studies of diacetylene polymerisation reactions present special interest. The first example of polyacetylene synthesis from a diacetylenic monomer has been described recently.²⁶³

The diacetylene present in industrial gases enters into reactions of nucleophilic addition selectively. In this review, it is these transformations which encompass only some of possible applications of diacetylene and its derivatives that are analysed in detail. Thus copolymers of diacetylenic glycols and their derivatives are used as a basis in the preparation of stereoregulatory membranes mimicking cell liposomes¹⁴ and thermochromic polymeric layers^{264,265} for laser image recording and observations over conformational transitions in polymers at ambient temperatures.

The role of compounds produced from diacetylene will be increasing with the development of new technologies. The synthesis of reagents based on diacetylene can be the first step towards its commercial utilisation. This, in turn, will give an impetus to the development of new procedures for the synthesis of a vast variety of useful compounds from inexpensive industrial raw materials using reactions discussed in the present review.²⁶⁶

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Direct fluorination of fullerenes[†]

O V Boltalina, N A Galeva

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Abstract. Data on the synthesis of a new class of fluorocarbon compound, fluorofullerenes, by reactions of C₆₀, C₇₀, their mixtures and higher fullerenes with molecular fluorine are surveyed. The physicochemical and thermodynamic properties are presented for pure C₆₀F₄₈, which is the only compound formed selectively in direct fluorination of C₆₀, and for fluorofullerene mixtures. The bibliography includes 70 references.

I. Introduction

Very few naturally occurring compounds of fluorine exist, these are primarily mineral inorganic compounds. The unique properties inherent in fluorine and its compounds^{1,2} have served as the basis for the development of new modern technologies and a large number of fluorine-containing materials both in organic and inorganic chemistry.^{3,4}

The interest in the reaction of molecular fluorine with the new form of carbon, *viz.*, fullerenes, is undoubtedly due to the widely known useful properties of the products of direct fluorination[‡] of graphite, such as high thermal stability (up to 400 °C) of graphite fluorides (CF)_n and (C₂F)_n, the possibility of using fluorine-intercalated graphites C_xF with high degrees of fluorination as cathodic materials for lithium batteries, as well as the good antifriction properties of these compounds.^{5,6}

On the one hand, the polyhedral clusters of carbon, fullerenes, can be regarded as inorganic compounds, as this is an allotropic modification of carbon. On the other hand, fullerenes can be placed among organic compounds, as their behaviour in chemical transformations is similar to that of unsaturated hydrocarbons. Formally, C₆₀ and C₇₀ fullerenes have 30 and 35 double bonds, respectively.

Owing to delocalisation of the π -electron density, fullerenes undergo both addition to the double bonds and electrophilic addition with the intermediate formation of charge transfer complexes and, eventually, various derivatives. The C₆₀ fullerene can add up to 24 chlorine or bromine atoms or methyl groups. As

the size of the functional groups being added decreases, their number increases; for example, hydrogenation of C₆₀ can result in C₆₀H₃₆.

What is the maximum number of addends in the case of fluorine? On the one hand, the van der Waals radius of fluorine (1.35 Å) is greater than that of hydrogen (1.2 Å), and on the other hand, fluorine forms stronger bonds with carbon. The authors of theoretical work^{7–9} published before experiments on hydrogenation and halogenation of fullerenes were carried out had predicted that the completely fluorinated fullerene C₆₀F₆₀ would be stable. However, in this case, the steric interaction of the adjacent fluorine atoms would result in elongation of the carbon–carbon bonds in the fullerene framework to 1.67 Å,¹⁰ as well as in a decrease in the C–F bond energy by 15% in comparison with that of the C–F bond in CF₄.¹¹ The authors of yet another theoretical work¹² noted that the formation of the C₆₀F₆₀ molecule is possible provided that steric strain is relieved by distortion of the carbon framework with retention of the icosahedral symmetry. It was anticipated that, owing to its unique spherical symmetry, perfluorofullerene would possess good lubricating properties, similarly to graphite fluorides. It did not take the experimenters too long to answer these questions, and as early as in 1991, the first study was published¹³ dealing with the synthesis of highly fluorinated fullerene by the reaction of C₆₀ with molecular fluorine. It was shown that addition of 36 (as in the reaction with hydrogen) or more fluorine atoms can occur. Thus, a new line of research, *i.e.*, studies on the fluorination of fullerenes, appeared in fluorine chemistry.

This review is aimed at generalisation of the literature data available since 1991 and the own author's results concerning fluorination of fullerenes with molecular fluorine. We intentionally limit ourselves to direct fluorination reactions. First, the reaction of F₂ with fullerenes drew the highest attention of researchers in 1991–96; these were the peak years in the activity of scientific groups in the USA, Great Britain, France and Japan, who were experienced in direct fluorination and possessed the corresponding experimental equipment. Second, direct fluorination reactions are well-developed technological processes that have been implemented in large-tonnage manufacture of various fluorine-containing products. If areas of fluorofullerene application demanding their production on a relatively large scale are

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[‡] The term 'direct fluorination' designates the reaction involving molecular fluorine, as it is generally accepted in the literature (see *e.g.* Ref. 4).

found, it is the reactions with molecular fluorine that can prove to be the most efficient and economically sound.

We leave the studies on the alternative methods for fullerene fluorination, including the reactions with fluorides of transition metals, noble gases, *etc.*, outside the scope of this review; these studies have been covered in recent reviews.^{14,15} The authors of almost all pioneering publications of the early 1990s used samples obtained by direct fluorination of C₆₀ or C₆₀/C₇₀ mixtures to study the physical and chemical properties of fluorofullerenes. On the other hand, despite the abundance of original works published in this period, neither detailed analysis of the results obtained nor coordination of the data obtained by different authors regarding the composition and properties of fluorination products have been carried out to date.

II. Synthesis of fluorofullerenes

1. Direct fluorination of C₆₀ and C₆₀/C₇₀

The first synthetic study¹³ on fullerene fluorination was carried out soon after the development of the procedure for their synthesis in macroscopic quantities. Selig *et al.*¹³ studied the fluorination of fullerenes using a Sartorius magnetic balance, which allowed them to detect the changes in the sample weight to within 0.1 mg. The samples were kept in a fluorine atmosphere for at least 20 h to attain a constant weight. The largest weight gain occurred within the first several minutes, after which the absorption of fluorine markedly retarded. The electron impact (EI) mass spectrum (70 eV) of the yellowish-brown reaction product with the composition F : C₆₀ = 38 (the composition was determined by measurement of the weight gain and by titrimetry) contained peaks corresponding to the C₆₀F_{30–44} molecules, the most intense peak being due to the C₆₀F₃₆ molecule. It should be noted that Selig *et al.*,¹³ who used an IR cell for the fluorination, observed accumulation of CF₄ during the reaction ($\nu_{C-F} = 1283 \text{ cm}^{-1}$). It was shown¹⁶ that fluorination of fullerenes with molecular fluorine is accompanied by side reactions to give perfluoroalkanes C_nF_{2n+2} ($n = 1-4$). The mass spectrum of a gas phase sample taken directly from the reactor zone during the experiment (Fig. 1) showed, in addition to the F₂⁺ ions, the presence of C_nF_k⁺ ions ($n = 1-4, k = 1-9$).

In 1991, a paper by Holloway *et al.*¹⁷ was published. Direct fluorination of C₆₀ fullerene at 70 °C was monitored for several days. Three to four days after the beginning of fluorination, the black C₆₀ powder underwent an abrupt colour change to dark-brown; this colour remained apparently unchanged for another three to four days and then abruptly changed to light-brown. Subsequent fluorination resulted in gradual decolourising of the sample to white eventually. The stepwise change in the colour of the powder during the reaction was considered as evidence for consecutive addition of fluorine atoms to the fullerene molecule. It was assumed that the two intermediates (dark- and light-brown) were stable, partially fluorinated fullerene derivatives, C₆₀F₆ and

C₆₀F₄₂, while the white powder was C₆₀F₆₀. The formation of C₆₀F₆₀ was proven by NMR spectroscopy [the ¹⁹F NMR spectrum contained one intense band with a chemical shift (δ) of -150.5 ppm]. On the other hand, analysis of the mass spectra of the white powder showed peaks corresponding to species with compositions ranging from C₆₀F₆ to C₆₀F₄₂; however, species with higher fluorine contents (> 42) were not found.

Tuinman *et al.*¹⁸ performed the fluorination of fullerenes in various temperature and time modes using reaction vessels made of different materials (Pyrex, quartz, steel). For example, the following procedure was described: through a tube with an inserted capillary containing the fullerene, helium was first passed at 160 °C at a flow rate of 50 ml min⁻¹ for two hours in order to remove traces of moisture and then fluorine was passed at a flow rate of 1 ml min⁻¹ together with helium. When the temperature was increased, no visible changes in the sample occurred until helium feeding to the reactor was stopped (at 210 °C); as this was done, the volume of the powder increased and its colour changed from black to yellow. Then the temperature was increased to 275 °C and fluorine was passed for additional 4 h (the temperature was not further increased because of the vigorous reaction of fluorine with quartz). According to mass spectroscopic data, the main products, *viz.*, white powders, were mixtures of fluorofullerenes C₆₀F_{38–46} (Fig. 2); however, no perfluorinated fullerene C₆₀F₆₀ was detected, the maximum degree of fluorination being 48 (the C₆₀F₄₈ molecule). It was noted that molecules containing more than 48 fluorine atoms were not formed upon longer treatment of fullerenes with fluorine.

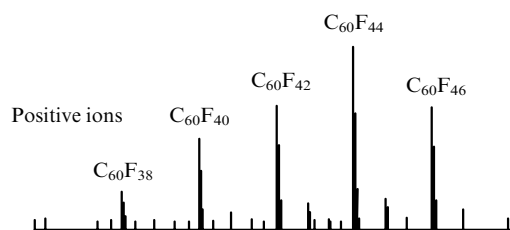


Figure 2. Electron impact mass spectra (70 eV) of a sample synthesised by Tuinman *et al.*¹⁸

Kniaz *et al.*¹⁹ monitored the course of C₆₀ fluorination using a Sartorius balance. The most intense peak in the mass spectrum of the air-stable yellowish-white reaction product corresponded to the C₆₀F₄₀ molecule. In addition, a 10⁻⁵ times less intense peak corresponding to the C₆₀F₆₀ molecule was observed. In order to improve the quality, the resulting product was sublimed at 300 °C; this gave a yellow sublimate and a white non-volatile residue which included black grains of amorphous carbon. Unlike the spectra of the starting sample, the mass spectra of the sublimate and the residue did not display peaks corresponding to the highly fluorinated C₆₀F_x molecules ($x > 48$). The absence of these peaks was explained by the liberation of molecular fluorine from C₆₀F_x ($x > 48$) during sublimation.

Okino *et al.*^{20–23} determined the composition of fluorofullerenes by X-ray photoelectron spectroscopy (XPS) in thin films obtained by deposition of C₆₀ on nickel plates which were then treated with fluorine under the same conditions as the C₆₀ powders (Table 1). The XPS data are in good agreement with mass spectroscopic data. For example, a sample with the composition F : C₆₀ = 45 (XPS data) contained C₆₀F₄₄ and C₆₀F₄₆ as the major components. It should be noted that the X-ray photoelectron spectra of the samples with low fluorine content (F : C₆₀ < 20) contained peaks belonging to the C₆₀ fullerene and C₆₀F_x fluorofullerene ($x \approx 40$) phases. It was assumed that even short-term fluorination converts a fraction of fullerene molecules to derivatives with high fluorine content, whereas the data of chemical analysis and XPS of the C₆₀F_x samples, where $x < 20$,

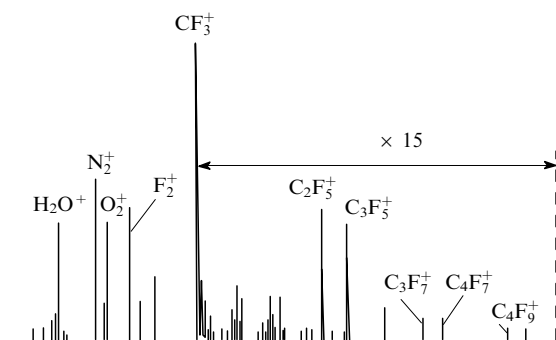


Figure 1. Mass spectra of a gas phase sample taken from the reactor during the reaction of fullerenes with molecular fluorine.

Table 1. Conditions used for the synthesis of fluorofullerenes and their characteristics.

C ₆₀ sample	Fluorination conditions			Reaction product according to data			Ref.
	time/h	T/°C	p/atm	CA	MS	XPS	
Film	4	200	1	—	C ₆₀ F _{42–46}	C ₆₀ F ₄₅	20
	24	150	1	—	—	C ₆₀ F ₄₀	20
	~288	70	1	—	—	C ₆₀ F ₂₀	20
	~336	70	1	C ₆₀ F ₉	—	C ₆₀ F ₂₂	20
Sample weight	4	200	—	C ₆₀ F ₄₅	—	—	21
	~672	200	—	—	—	—	21
See ^a	30	48–72	225 ^b	—	C ₆₀ F ₄₅	C ₆₀ F _{44–48}	22
	48	100	—	—	—	—	23

Note. The following designations are used: CA is chemical analysis; MS is mass spectroscopy; XPS is X-ray photoelectron spectroscopy. ^a Sample weight 30 mg; ^b mm Hg.

showed only the presence of unreacted C₆₀ together with highly fluorinated molecules.

Hamwi *et al.*^{24,25} fluorinated C₆₀ using a setup made of Monel and steel. A fullerene powder was placed in an aluminium boat; the reaction was carried out at 20–300 °C, either under static conditions ($p = 1–5$ atm) or in a stream of fluorine (the flow rate was 2 ml min^{−1}) for 10–336 h. Thermogravimetric analysis showed that fluorofullerenes started to decompose at 180 °C. For this reason, the reaction at temperatures above 180 °C was stopped at the instant when the product weight started to decrease. This resulted in a series of differently coloured powders (from black to pale yellow). The maximum weight gain recorded for one of the samples corresponded to the stoichiometry F:C₆₀ = 58.5. On the other hand, without mass spectroscopic analysis, it is difficult to make reliable conclusions on the actual presence of molecules with such a high fluorine content.

Short-term reactions of the same compounds gave fluorofullerenes with low fluorine stoichiometric factors (*e.g.*, C₆₀F₉), as determined from weight gain. According to IR spectroscopic and X-ray diffraction data, these samples contained only the non-fluorinated fullerene, while the ¹⁹F NMR spectrum exhibited one broad peak, which proved the presence of fluorine in the products.²⁵

It was found^{24,25} that C₆₀/C₇₀ fullerene mixtures are more reactive than C₆₀ fullerene. For example, the reaction of C₆₀/C₇₀ with fluorine at room temperature for 4 h resulted in an increase in the sample weight; however, the weight of pure C₆₀ samples did not change upon longer treatment (48 h) under the same conditions. Fluorination of C₆₀/C₇₀ at 300 °C for 4 h afforded a pale

yellow product with the ratio F:C₆₀ = 44, whereas for pure C₆₀, it took 8 h to attain the same degree of fluorination.

Bagryantsev *et al.*¹⁶ fluorinated a C₆₀/C₇₀ fullerene mixture and found that if the reaction temperature is raised from 70 to 315 °C, the content of fluorofullerenes with higher degrees of fluorination gradually increases. The C₆₀F_x ($x = 38, 40$) and C₆₀F₄₈ fluorofullerenes were the main components among the products obtained at 70 and 315 °C, respectively. The trend towards higher degrees of fluorination at elevated temperatures was also observed in the case of C₆₀ fullerene (Table 2). For example, the C₆₀F₄₆ fluorofullerene with a small admixture of C₆₀F₄₄ and C₆₀F₄₈ was the main reaction product at 275 °C. Fluorination of C₆₀ at 315 °C under dynamic conditions resulted in a mixture of fluorofullerenes, in which C₆₀F₄₈ was the major product, C₆₀F₄₆ was a minor product, whereas the content of C₆₀F₄₄ was insignificant. Figure 3 shows a diagram demonstrating the effect of fluorination time of C₆₀ at 315 °C on the C₆₀F₄₈ content in the resulting samples. Repeated fluorination increased the C₆₀F₄₈:C₆₀F₄₆ ratio but also resulted in an appreciable loss of the original fluorofullerene due to thermal destruction (partial burning and sublimation); according to mass spectroscopic data, the content of the main product (C₆₀F₄₈) was as high as 95%. Fluorination at higher temperatures (up to 355 °C) for 2–3 h resulted in ~90% of C₆₀F₄₈; the reaction yield was > 80% in most cases. This procedure was beneficial regarding the reaction time and the consumption of reactants.

A study of the effect of the method of feeding fluorine to the reactor showed that the reaction under dynamic conditions in the absence of flashes mostly gave two components, *viz.*, C₆₀F₄₈ and

Table 2. Experimental data on the fluorination of fullerenes with molecular fluorine and composition of the products obtained.¹⁶

Starting compound	Mode	T _{max} /°C	ω (%) ^a	Ratio F:C ₆₀ in the products according to data				Composition according to mass spectroscopy data			
				see ^b	CA	XPS	NMR	C ₆₀ F ₄₄	C ₆₀ F ₄₆	C ₆₀ F ₄₈	F:C ₆₀ (see ^c)
C ₆₀ (see ^d)	dynamic	275	94	43	46 ± 1	—	46.0 ± 0.5	16	77	4.3	45.77
C ₆₀	quasi-static	315	70	22	44 ± 1	44 ± 2	—	19	50	13	45.45
C ₆₀ F _x ^e	"	315	—	—	—	—	—	3.2	32	63	47.23
C ₆₀ F _x ^e	static	315	—	—	—	—	—	6.9	33	51	46.40
C ₆₀ F _x ^e	dynamic	315	—	—	48 ± 1	46 ± 2	—	0	3.8	95	47.92
C ₆₀	"	315	56	10	48 ± 1	—	—	14	33	49	46.53
C ₆₀	"	315	88	38	49 ± 1	—	—	1.5	29	68	47.37
C ₆₀ (see ^d)	"	340	88	37.4	—	—	—	0	13	85	47.74
C ₆₀ (see ^d)	"	340	80	31.1	—	—	—	0	10	88	47.79
C ₆₀	"	350	51	6.1	49 ± 1	—	—	0	6.3	91	47.87
C ₆₀	"	350	84	34	—	—	48.0 ± 0.5	4.7	12	81	47.52

^a The reaction yield (ω) was calculated using the formula: $\omega = (m_{\text{exp}}/m_{\text{theor}}) \times 100\%$, where m_{exp} and m_{theor} are the C₆₀F₄₈ masses; ^b the calculation is based on the weight gain; ^c the measurement accuracy is ±0.02; ^d F₂ diluted with 90 vol.% Ar was used; ^e the fluorination of fluorofullerenes C₆₀F_x was carried out successively in quasi-static, static and dynamic modes.

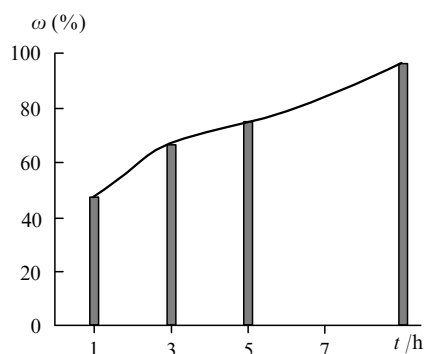


Figure 3. Effect of time (t) of C_{60} fluorination with molecular fluorine at $315\text{ }^{\circ}\text{C}$ on the $C_{60}F_{48}$ content (ω) in the samples synthesised.

$C_{60}F_{46}$. The product obtained under quasi-static conditions (Fig. 4) contained $C_{60}F_x$ fluorofullerenes, where $x = 40\text{--}48$, and an admixture of the $C_{60}F_{44}O$ and $C_{60}F_{46}O$ oxyfluorides (empirical formula $C_{60}F_{45.45}O_{0.05}$). It is evident from Fig. 4 that the absorption of fluorine at low temperatures (up to $110\text{ }^{\circ}\text{C}$) virtually does not occur (section I). In section II, starting from $110\text{ }^{\circ}\text{C}$, noticeable fluorine absorption at a specified, constant rate of heating was observed. The rate of fluorine absorption in the temperature range from 160 to $311\text{ }^{\circ}\text{C}$ (section III) was almost constant. When the temperature was maintained constant (section IV, $315\text{ }^{\circ}\text{C}$), noticeable fluorine absorption ceased.

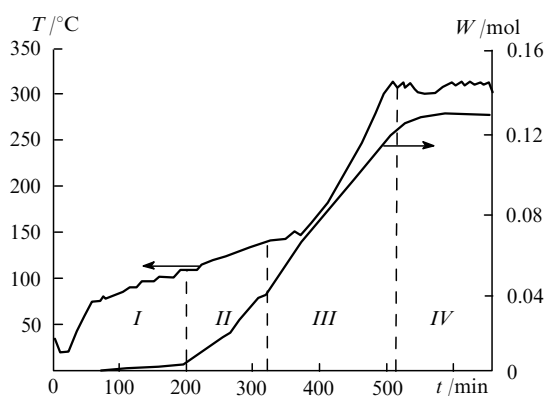


Figure 4. Changes in the temperature and in the fluorine amount absorbed (W) during the fluorination of C_{60} under quasi-static conditions.

Matsuo *et al.*²⁶ fluorinated C_{60} using various methods: with molecular fluorine, with a mixture of fluorine and hydrogen fluoride, with molecular fluorine under UV irradiation, and by passing a stream of fluorine through a $CFCl_3$ solution of fullerene (Table 3). The last-mentioned technique, which is the only reported example of liquid-phase fluorination where a low degree of fluorination is attained, might be a promising method for the

synthesis of fluorofullerenes with low fluorine contents. However, the methods which were used to analyse the products do not allow unambiguous conclusions to be made about the actual molecular composition of the fluorides, in particular, about the formation of products with low fluorine content. In general, the molecular formulae established for the fluorofullerenes were in agreement with the data reported by other investigators. For example, the largest degree of fluorination was attained when UV irradiation was used (see also the data in Ref. 27).

Chilingarov *et al.*²⁸ studied C_{60} fluorination under conditions of a mass spectroscopic experiment where molecular fluorine was fed from a cylinder into an effusion cell. The temperature ($500\text{--}800\text{ K}$) and the reaction time, as well as the fluorine pressure ($10^{-4}\text{--}10^{-5}\text{ atm}$) were varied. In the F_2 (gas)– C_{60} (solid) system, only molecules with an even number of fluorine atoms, $C_{60}F_{2n}$ ($2 < 2n < 44$), were formed. The composition of the gas phase was largely temperature-dependent: an increase in temperature shifted the distribution of ions in the mass spectrum towards smaller masses. For example, the following major products were obtained: $C_{60}F_{38}$ at 510 K , $C_{60}F_8$ at 760 K , and $C_{60}F_2$ and $C_{60}F_4$ at 800 K . Longer reaction times at 745 and 800 K increased the content of $C_{60}F_{18}$ and $C_{60}F_{22}\text{--}C_{60}F_{46}$, respectively. A search for conditions for selective synthesis of a certain fluorofullerene in the gas phase was performed. For example, the maximum yield of $C_{60}F_{18}$ (50%) was attained if the reaction was carried out for 20 h at 720 K and at a fluorine pressure of $2 \times 10^{-4}\text{ atm}$ in the presence of NiF_2 . In the presence of MnF_2 (10 h , 615 K , $p_{F_2} = 2 \times 10^{-4}\text{ atm}$), up to 90% of $C_{60}F_{36}$ was formed. No study of solid-phase fluorination products, which could be obtained, *e.g.*, by condensation from the gas phase, was carried out.²⁸ Therefore, it is impossible to estimate the applicability of the above approach for the selective synthesis of macroscopic quantities of fluorofullerenes.

Thus, the studies on direct fluorination of fullerenes described in this Section showed that

(1) the reaction with molecular fluorine occurs readily and the products of fullerene fluorination can form even at room temperature;

(2) as a rule, mixtures of fluorofullerenes $C_{60}F_n$ with a wide range of compositions are formed ($9 \leq n \leq 54$, see Ref. 25); the samples with fluorine content $n < 36$ are mixtures of highly fluorinated products ($36 \leq n \leq 48$) and unreacted C_{60} (the higher the content of the latter in the mixture, the smaller the stoichiometric coefficient for the fluorine atom);

(3) fluorofullerene molecules from $C_{60}F_2$ (see Ref. 28) to $C_{60}F_{102}$ were detected in the gas phase.²⁷

The studies were carried out in the temperature range of $20\text{--}300\text{ }^{\circ}\text{C}$ (on increasing the temperature above $300\text{ }^{\circ}\text{C}$, either no noticeable weight gain in the sample occurred or fluorine reacted vigorously with the reactor material); $C_{60}F_{44}$ and $C_{60}F_{46}$ were the main fluorination products at $275\text{--}300\text{ }^{\circ}\text{C}$.¹⁶

2. Fluorination of fullerene bromo and chloro derivatives

In order to obtain fullerene derivatives with low fluorine content, an attempt was made to fluorinate bromo and chloro fullerene derivatives such as $C_{60}Br_{24}$, $C_{60}Br_8$, $C_{60}Br_6$ and $C_{60}Cl_{24}$ with

Table 3. Conditions of the synthesis of fluorofullerenes from C_{60} and their characteristics.²⁶

Fluorinating agent	Time /days	$T/^{\circ}\text{C}$	Ratio F : C_{60} in the products according to data			Product colour
			see ^a	CA	XPS	
F_2	11.5–27	20–90	40	41	45	—
$F_2\text{--HF}$	12–35	20–85	—	42–45	—	—
F_2 under UV irradiation (254 nm)	11–14	20–70	> 45	47–52	—	yellowish-white
F_2 (see ^b)	0.2–14	20–65	—	27–33	—	—

^a The calculation is based on the weight gain; ^b the stream of fluorine was passed through a $CFCl_3$ solution of C_{60} ;

molecular fluorine.²⁹ The idea was to perform the reaction in two stages: in the first step, fluorine had to add to the carbon atoms unoccupied by bromine or chlorine, while in the second stage, due to the lower strength of the C–Cl and C–Br bonds with respect to the C–F bond, abstraction of Br₂ and Cl₂ on heating was expected giving rise to fluorofullerenes with a low fluorine content. However, the reaction of C₆₀Br₂₄ with molecular fluorine resulted in complete displacement of bromine even without additional heating to give fluorofullerenes with variable composition up to C₆₀F₄₄ with predominant formation of C₆₀F₃₆. Fluorination of C₆₀Br₈ gave C₆₀F₃₆; the resulting product contained mostly C₆₀F₁₈ as well as mono- and dioxides of fluorofullerenes. As in the reaction of C₆₀ fullerene with gaseous fluorine, fluorine compounds with an even number of fluorine atoms in the molecule were formed.

3. Synthesis of pure fluorofullerenes by direct fluorination

The use of the reaction of C₆₀ with molecular fluorine for the synthesis of fluorofullerenes with a particular number of fluorine atoms was first reported by Gakh *et al.*³⁰ Fluorination was carried out in two stages. A stream of molecular fluorine ($v = 1.3 \text{ ml min}^{-1}$) was passed over a mixture of C₆₀ with NaF at 250 °C for 20 h, then the product was extracted with CFCl₃ and dried; a new portion of NaF was added, and the mixture was again treated with a stream of F₂ (275 °C, 30 h). After extraction and drying, the composition of the sample was determined by mass spectroscopic analysis using field desorption for ionisation. The intensity of the ion corresponding to the C₆₀F₄₈ molecule was 69% of the overall intensity of the ions corresponding to the C₆₀F_{2n} molecules ($2n \leq 48$). A study of the ¹⁹F NMR spectrum of a sample with a sufficiently high content of C₆₀F₄₈ allowed the researchers to suggest the molecular structure of C₆₀F₄₈ (see Section III.5).

Considerable progress^{16,31,32} in the synthesis of pure C₆₀F₄₈ (with > 95% of C₆₀F₄₈ in the samples) was attained in studies of the dependence of the composition of the products of C₆₀ fluorination with molecular fluorine on the temperature (70–355 °C) and on the reaction conditions. At each intermediate step before the next increase in the temperature, the molecular composition was determined by high-temperature mass spectroscopy with electron impact ionisation and evaporation of samples from the effusion cell. The fluorination products had the form of white powders stable in air for at least three years. The molecular structure of the C₆₀F₄₈ fluorofullerene obtained by this method was identical to that reported by Gakh *et al.*³⁰

4. Fluorination of C₇₀ and higher fullerenes

The fluorination of C₆₀/C₇₀ mixtures resulted in a series of products C₇₀F_n, where $n = 48$ (see Ref. 24) and 54 (see Ref. 18) for the components with the maximum degree of fluorination. The reaction of pure C₇₀ with fluorine resulted in mixtures of fluorides containing mainly C₇₀F₄₀ (see Ref. 13), C₇₀F₃₈ (see Ref. 16) and C₇₀F₅₄ (see Ref. 31). In these mixtures, C₇₀F₄₆ (see Ref. 13), C₇₀F₄₈ (see Ref. 16) and C₇₀F₅₆ (see Ref. 31), respectively, had the maximum degrees of fluorination. Experiments carried out successively at 250, 280 and 350 °C showed an increase in the degree of fluorination with increase in temperature. However, even at 350 °C, the fluorination product was a mixture of compounds from C₇₀F₃₈ to C₇₀F₅₆ (Fig. 5).¹⁶

The only reference to the fluorination of higher fullerenes with molecular fluorine can be found in the paper by Bagryantsev *et al.*³¹ The mass spectrum of the product of fluorination of a fullerene mixture containing small amounts of C₇₆ and C₈₄ showed the presence of C₇₆F₅₄ and C₈₄F_n ($n = 56–62$). The reaction was carried out under the same conditions as the fluorination of C₇₀ to give C₇₀F₅₆.³¹

Thus, the maximum number of fluorine atoms that can be added to C₆₀ and C₇₀ (48 and 56, respectively) corresponds to 80%

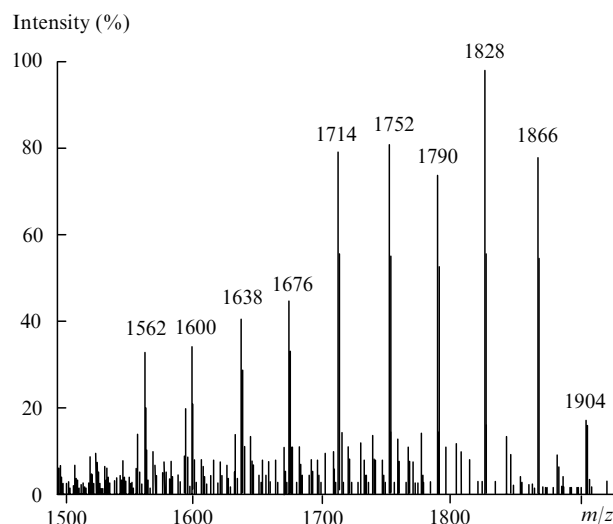


Figure 5. Electron impact mass spectrum of a C₇₀F_n sample ($n = 38–56$) synthesised at 350 °C. The maximum degree of fluorination corresponds to C₇₀F₅₆ (1904 amu) and the most intense peak corresponds to 1828 amu, i.e., C₇₀F₅₂.

occupation of the reaction sites in fullerene molecules. More extensive fluorination on treatment of fullerenes with molecular fluorine at temperatures of up to 350 °C is probably hampered by the inaccessibility of the remaining double C=C bonds because of steric hindrance caused by the size of the fluorine atoms and the rigidity of the spherical carbon skeleton. Pure fluorides of the C₇₀ fullerene will probably be hardly accessible due to the lower symmetry of C₇₀ in comparison with C₆₀. In the case of heavy fullerenes, the prospects for the synthesis of pure compounds are also complicated by the existence of geometrical isomers.

III. Methods of study and physical properties of fluorofullerenes

1. IR spectroscopy

The IR spectroscopic data for fluorofullerenes are reported in many papers. As the compositions of fluorofullerene samples are known, one can follow a correlation between the vibration frequency of the C–F bonds and the fluorine content in the samples. For example, the broad unresolved band at 1148–1165 cm^{−1} typical of fluorofullerene mixtures C₆₀F_x ($36 \leq x \leq 48$)^{13,19} shifts towards 1170–1176 cm^{−1} for the pure C₆₀F₄₈ fluorofullerene.¹⁶ A similar shift of bands with increase in the fluorine content was also observed in the case of fluorinated graphite: 1110–1120 cm^{−1} for fluorine-intercalated graphite with the composition C₂F (see Ref. 26) and 1220 cm^{−1} for graphite fluorides (CF)_n, (C₂F)_n.^{33,34}

The main distinction of the IR spectra of pure C₆₀F₄₈ from those of fluorofullerene mixtures is that fine structure in the region of C–F vibrations and a group of intense bands in the region of 600–800 cm^{−1} are displayed (see Refs 26, 32). One can see in Fig. 6 that the most intense peaks at 650 and 723 cm^{−1} are characteristic only of the C₆₀F₄₈ fluorofullerene but are absent from the IR spectrum of a C₆₀F₄₆ sample. Evidently, the bands in this spectrum region can serve as ‘fingerprints’ of pure C₆₀F₄₈. The IR spectra for certain C₆₀F₄₈ isomers were calculated in a theoretical study,³⁵ but no detailed assignment of the normal vibration modes has been carried out to date.

IR spectroscopic data for some C₆₀F_x fluorofullerene samples are presented in Table 4.

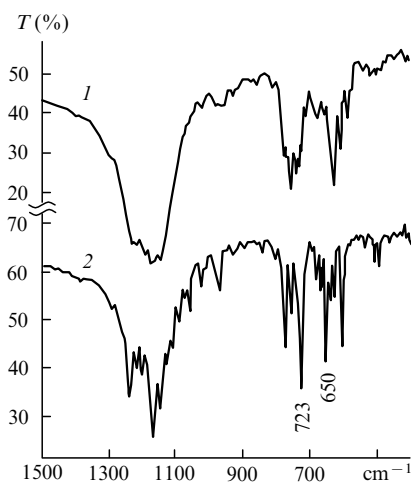


Figure 6. IR spectra of fluorofullerene samples: $C_{60}F_{46}$ (1) and $C_{60}F_{48}$ (2).³²

Table 4. IR spectroscopic data for some samples of $C_{60}F_x$ fluorofullerenes.

x	Vibration frequencies / cm^{-1}	Ref.
36 (see ^a)	1164, 1133	34
$6 \leq x \leq 42$	1148	17
$38 \leq x \leq 48$	1150, 750, 510	18
$30 \leq x \leq 44$	1165	13
47	1168	24
27–52	1150, 750, 600	26
48	1170, 1141, 755, 736, 723, 650, 604	31

^a The fluorofullerene was synthesised in the reaction with manganese trifluoride.

2. Electronic structure and electrochemical properties

The electronic structure of fluorinated fullerenes differs from the electronic structure of the original fullerenes. The high electronegativity of fluorine decreases both the LUMO and the HOMO energies, thus the electron affinity and the first ionisation potential of $C_{60}F_x$ and $C_{70}F_x$ increase in comparison with those of C_{60} and C_{70} . Obviously, the changes in the electronic potentials occurring due to transformation of fullerenes to fluoro derivatives affect their electrochemical and photoelectrochemical behaviour. Data on the electronic structures of the $C_{60}F_{48}$ and C_{60} molecules obtained by XPS, from the near fine structure and from the near-edge X-ray absorption fine structure spectra (NEXAFS) are presented in Fig. 7.

It was found³⁶ that the work functions for $C_{60}F_x$ are 5.6, 5.2 and 5.4 eV for $x = 30, 36$ and 48, respectively. This is considerably higher than the work functions for organic compounds (usually, 4.1–5.0 eV) and for C_{60} fullerene (4.7 eV³⁹), which points to strong electron-withdrawing properties of fluorofullerenes.

The addition of fluorine to fullerene shifts the bands in the absorption spectra from 1.8 eV for C_{60} fullerene to 6.4 eV for $C_{60}F_x$ ($42 \leq x \leq 48$).⁴⁰

Many researchers have studied fluorofullerenes by XPS,^{25,26,41–43} but the data of different authors are in poor agreement due to the use of different types of X-ray radiation, different calibrations of the instruments and different substrate materials. In certain cases, surface charging and a shift of the absolute energy scale were observed, which complicated considerably the interpretation of the spectra and made it difficult to obtain reliable data on the composition of the fluorofullerene samples and on the chemical shifts. According to some data of

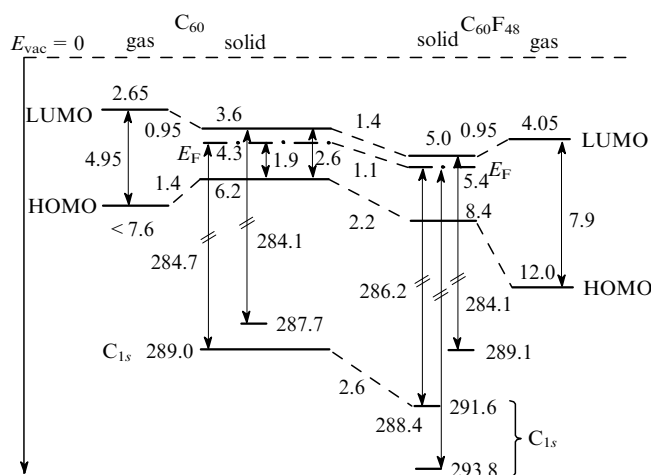


Figure 7. Energy diagram for the C_{60} and $C_{60}F_{48}$ molecules in the gas and solid phases³⁶ (the HOMO value was changed in accordance with the data in Refs 37 and 38).

multicomponent photoelectron C_{1s} spectra,^{22,25,41,42} destruction processes take place on a sample surface exposed to hard X-radiation, which is accompanied by a flow of high-energy electrons. In addition, it was found²⁶ that the relative intensity of peaks in the photoelectron spectra depended on the duration of the exposure of samples to X-radiation. This was explained by the destructive effect of the electron flux. For example, according to the data reported by Matsuo *et al.*²⁶ the $C_{60} : F$ ratio was 42 after irradiation of a fluorofullerene sample for 33 s, while an increase in the irradiation time to 750 s decreased the content of fluorine to $C_{60} : F = 38$.

The use of electron-free synchrotron radiation (40–500 eV) made it possible to prevent the destruction of the fluorofullerene surface layer and to eliminate the charge accumulation on the sample surface. The photoelectron spectra obtained under these conditions⁴³ displayed peaks at 287.2 and 284.9 eV, which were interpreted as the energies of the $1s$ electrons of the carbon atoms (E_b) involved in the formation of the C–F and C–C bonds, respectively (Fig. 8a). Similar two-component C_{1s} spectra were also obtained in other studies.^{26,36,45,46} The two lines in the F_{1s}

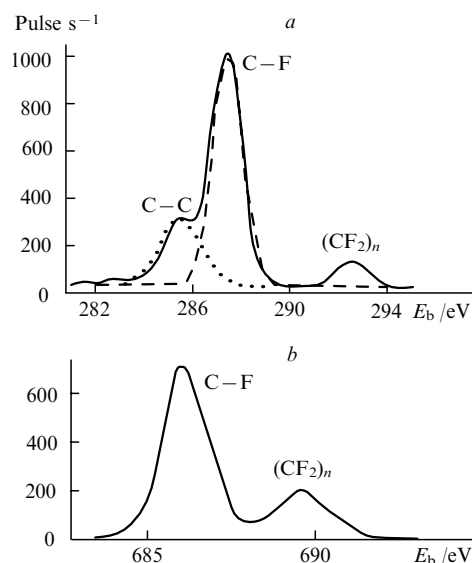


Figure 8. X-Ray photoelectron spectra of $C_{60}F_{48}$: (a) spectrum of carbon $1s$ electrons; (b) spectrum of fluorine $1s$ electrons excited by X-ray radiation of $AlK\alpha_{1,2}$ with Teflon as the standard.⁴⁴

photoelectron spectrum of $C_{60}F_{48}$ fluorofullerene (Fig. 8b) at 685.9 and 689.5 eV represent two states of fluorine, namely, those in fluorofullerene and in Teflon, respectively.

In certain studies, the XPS method was used to determine the compositions of the samples obtained (see Tables 1, 2). However, the accuracy of these estimates is insufficient, ± 2 fluorine atoms per fullerene molecule.

It is well known that, depending on the fluorine content in fluorine-intercalated graphite C_xF , the nature of the C–F bond changes from ionic to partially ionic (or partially covalent).⁵ The F_{1s} photoelectron spectra of C_xF compounds with low fluorine content display one peak at 684.5 eV; this corroborates the existence of only one type of fluorine atoms in the compound, which are in the same electronic state as those in metal fluorides (for instance, the peak at 685.6 eV represents LiF^{22}). It is believed⁵ that intercalated fluorine atoms distributed between carbon layers undergo ionisation and interact with the $C_x^{\delta+}$ polycation.

The increase in x in C_xF to 10 is accompanied by some delocalisation of the electron density, hence the C–F bond cannot be considered as purely ionic. The F_{1s} spectrum displays a peak at 685.7–685.8 eV. Subsequent increase in the fluorine content in C_xF produces a second peak in the C_{1s} spectrum, which is explained by a covalent contribution to the energy of the fluorine–carbon bond. Thus, the C_xF compounds with the composition $2 \leq x \leq 4$ contain fluorine–carbon bonds of two types: ionic and partially ionic (or partially covalent). The observed chemical shifts in the photoelectron spectra are listed in Table 5.

Matsuo *et al.*²⁶ compared the photoelectron spectra of fluorofullerene, fluorine-intercalated graphite C_2F and graphite fluorides $(C_2F)_n$ and $(CF)_n$ (Fig. 9). It is important that the high-energy peak for $C_{60}F_{43}$ fluorofullerene (291.1 eV) is located approximately between the corresponding peaks of C_2F and graphite fluorides, whence the authors conclude that the degree of covalency of the C–F bond in fluorofullerene is intermediate between those of the C–F bonds in C_2F intercalates and in graphite fluorides.

The differences between the electron binding energies (ΔE_b) in carbon atoms with different chemical environments were compared;²⁶ the difference is manifested in the C_{1s} photoelectron spectra as two peaks. It was concluded that the greater ΔE_b , the

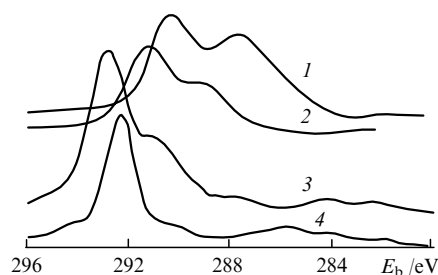


Figure 9. X-Ray photoelectron spectra of carbon $1s$ electrons in fluorine-intercalated graphite C_2F (1), $C_{60}F_{43}$ fluorofullerene (2) and graphite fluorides $(C_2F)_n$ (3) and $(CF)_n$ (4).²⁶

more ionic and less covalent the C–F bond. For example, ΔE_b for $C_{60}F_{33}$ and $C_{60}F_{31}$ samples is smaller than that for fluorine-intercalated graphite C_2F and larger than that for graphite fluoride $(C_2F)_n$, which suggests that the C–F bond in fluorofullerene has an intermediate character between covalent and semi-ionic. Comparison of the ΔE_b values in the C_{1s} spectra in $C_{60}F_{48}$ fullerene (1.8 eV) and in the spectra of fluorine-intercalated graphite (2.6 eV) and graphite fluorides (1.9 eV) showed that the C–F bond in $C_{60}F_{48}$ is covalent. The average ΔE_b values were 2.2–2.4 eV (see Table 5).

The electrochemical behaviour of fluorofullerenes was first studied by cyclic voltammetry. Holloway *et al.*¹⁷ studied the electrochemical reduction of $C_{60}F_{48}$ in a CH_2Cl_2 solution and detected the reaction products using a mass spectrometer. It was shown that the reduction of $C_{60}F_{48}$ occurs reversibly and that the reduction potential of $C_{60}F_{48}$ is 1.38 V higher than that of C_{60} . This agrees completely with the fact that the electron affinity of fluorinated fullerenes is about 1.5 eV higher than that of fullerenes. Based on the mass spectra obtained using the electro-spray method, it was concluded⁴⁷ that the electrochemical reduction mechanism includes a series of consecutive reactions of electron transfer and abstraction of fluorine atoms.

A study of the electrochemical properties of fluorofullerenes in solid electrolytes based on polyphosphazene derivatives doped with Li^+ was carried out.⁴⁸ The cathodic mixture contained a fluorofullerene, graphite and the electrolyte in the mass ratio

Table 5. X-Ray photoelectron spectroscopy data for fluorine-intercalated graphite, graphite fluorides and fluorofullerenes.

Compound ^a	$E_b(F_{1s})$ /eV	$E_b(C_{1s})$ /eV		$\Delta E_b(C_{1s})$ /eV	Ref.
		C–C	C–F		
C_xF ($20 < x$)	684.5	284.6	—	—	5
C_xF ($4 < x < 10$)	685.7–685.8	284.1	—	—	5
C_xF ($2 \leq x \leq 4$)	686.0–687.1	284.1–284.6	286.8–288.0	2.7–3.4	5
C_2F	687	287.5	290.1	2.6	26
C_4F	—	283.4	286.6	3.2	26
$(C_2F)_n$	690	290.8	292.7	1.9	26
$(CF)_n$	689.6	—	290.4	—	33
C_{60}	—	284.6	—	—	22
C_{60}	—	284.7	—	—	37
$C_{60}F_{48}$	—	286.2	288.4	2.2	37
$C_{60}F_x$ ($x = 44, 46, 48$)	—	284.9	287.2	2.3	43
$C_{60}F_{47}$	—	288.5, 290.7, 293.3	—	—	26
$C_{60}F_{43}$	—	288.9	291.1	2.2	26
$C_{60}F_x$ ($x = 31, 33$)	—	288.0	290.4	2.4	26
$C_{60}F_x$	688	284.6	289.5	4.9	42
$C_{60}F_{48}$	—	291.5	293.5	2.0	45
$C_{60}F_{48}$	685.9	285.6	287.4	1.8	46
$C_{60}F_x$ ($x = 40–48$)	—	286.8	289.3	2.5	46

^a The sample composition is given in accordance with original work.

1 : 1 : 2. The voltammograms of $C_{60}F_x$ and $C_{70}F_x$ fluorofullerenes in solid-phase lithium batteries showed peaks at potentials of 3.1 and 3.4 V relative to the $E(\text{Li}^+/\text{Li})$ potential, which corresponded to irreversible reduction of $C_{60}F_x$ and $C_{70}F_x$. After two voltammetric cycles, XPS showed a decrease in the relative intensity of the signal at 289 eV in the C_{1s} spectrum for the carbon atoms involved in the C–F bonds and the appearance of a new signal at 685 eV in the F_{1s} spectrum. This is evidence for irreversible reduction of C–F bonds during the experiment and the formation of LiF. Similar experiments with fluorinated graphite $(\text{CF})_n$ showed that its reduction potential is 0.5 V more negative than that of fluorofullerene. This implies that the C–F bond in the $C_{60}F_x$ molecule is reduced more readily than the C–F bond in $(\text{CF})_n$. It was assumed that reduction of fluorofullerenes under galvanostatic conditions is homogeneous, unlike the heterogeneous reduction of graphite fluoride $(\text{CF})_n$.

The electrochemical behavior of fluorofullerenes the synthesis of which is described in Section II and Table 3 was studied as a function of the elementary composition (from $C_{60}F_{15}$ to $C_{60}F_{47}$).⁴⁹ It was shown that the reduction potentials of fluorofullerenes approach the reduction potential of C_{60} fullerene as the fluorine content decreases.

3. Crystal structure

The structure of C_{60} fullerene at room temperature is described by a face-centred cubic (FCC) lattice with the parameter $a = 14.17 \text{ \AA}$; the distance between the neighbouring C_{60} molecules is $10.02 \text{ \AA}$, and the density is 1.72 g cm^{-3} (which corresponds to $1.44 \times 10^{21} \text{ molecules cm}^{-3}$).¹⁰

Data of numerous X-ray diffraction studies (see, *e.g.*, Refs 19, 20, 50–53) indicate that at room temperature, the products of fullerene fluorination have the same FCC lattice (Table 6) as the matrix compound C_{60} but with an increased spacing. The increase in the distance between two neighbouring molecules following fluorination manifests itself as a shift of diffraction lines to smaller reflection angles: the first maximum is at $2\theta = 9^\circ$,¹³ which is much smaller than for crystalline C_{60} . Some papers reported the absence of crystallinity, especially for samples obtained at rather low temperatures.^{20, 24, 25} The diffraction pattern usually contained two diffuse peaks indicating the absence of long-range order, characteristic of crystals.

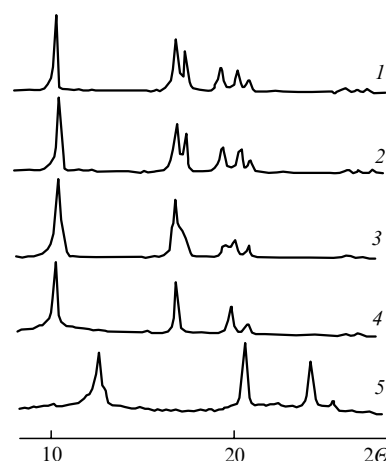


Figure 10. X-Ray diffraction patterns of samples with increasing contents of $C_{60}F_{48}$ (1–3), $C_{60}F_{46}$ fluorofullerene (4) and C_{60} fullerene (5).⁴⁶

The a parameters for fluorofullerene samples obtained by different research groups and described by a FCC lattice range from 16.98 (see Ref. 20) to $17.6 \text{ \AA}$,²⁴ which approximately corresponds to an increase in the molecular volume by a factor of 1.8 relative to that of C_{60} .⁵⁰

Due to the replacement of the short double bonds by longer single bonds, the radius of the carbon cage in a fluorofullerene molecule increases by 1% (from 3.53 to $3.56 \text{ \AA}$)⁴⁷ with respect to that of C_{60} , or by 10% according to other data.²¹ Representing a fluorofullerene molecule by two concentric spheres which correspond to the positions of the carbon and fluorine atoms (the C–F bond length is $1.36 \text{ \AA}$) and considering that fluorination results in an increase in the radius of the carbon cage by 10%, Okino *et al.*²¹ calculated the X-ray spectra for $C_{60}F_{45}$ and $C_{70}F_{32}$ samples.

Kniaz *et al.*^{19, 51} studied a sublimed fluorofullerene powder; the most intense peak in its mass spectrum was that of $C_{60}F_{40}$. It was shown that it contained 60% of a FCC phase and 40% of a hexagonal phase (see Table 6) and had a higher degree of crystallinity than unsublimed fluorofullerene.

Table 6. Lattice parameters, the number of molecules in a unit cell and the density of fluorofullerenes at room temperature.

Compound	Lattice type	Lattice parameters / $\text{\AA}$		z	$V_{\text{cell}}/z / \text{\AA}^3$	$d_{\text{calc}}^a / \text{g cm}^{-3}$	Ref.
		a	c				
C_{60}	FCC	14.17		4	711	1.681	10
$C_{60}F_{45}$ (see ^b)	FCC	17.07		4	1250	2.093	20
$C_{60}F_{40}$ (see ^b)	FCC	16.98		4	1224	2.009	20
$C_{60}F_{20}$ (see ^b)	FCC	17.3		4	1294	1.412	20
$C_{60}F_{22}$ (see ^b)	FCC	17.3		4	1294	1.412	20
$C_{60}F_{54}$ (see ^c)	FCC	17.60 ± 0.15		4	1363	2.128	24
$C_{60}F_{33}$ (see ^b)	FCC	17.21		4	1274	2.252	25
$C_{60}F_{48}$	FCC	17.27		4	1288	2.105	47
$C_{60}F_{40}$ (see ^d)	BCT-40%	11.85	19.28	2	1354	—	19, 51
	FCC-60%	16.677		4	1160	—	19, 51
$C_{60}F_{46}$ (see ^d)	FCC	17.158(3)		4	1263	2.096	46
$C_{60}F_{48}$ (see ^d)	BCT	11.852(8)	17.91(1)	2	1258	2.155	46
	FCT	16.75	17.9	4	1256	2.096	46
$C_{60}F_{48}$ (see ^d)	BCT	11.859(3)	17.83(2)	2	1254	2.162	52
$C_{60}F_{46}$ (see ^d)	FCC	17.24(1)		4	1281	2.116	52
$C_{60}F_{48}$ (see ^d)	orthorhombic	12.06(3) ^e	12.21(4)	1	1398	1.939	53

Note. The following designations are used: FCC is face-centred cubic lattice, BCT is body-centred tetragonal lattice, and FCT is face-centred tetragonal lattice; ^a $d_{\text{calc}} = M/(VN_A)$, where M is molecular mass, V is the cell volume, N_A is the Avogadro number; ^b composition was determined by photoelectron X-ray spectroscopy; ^c composition was determined from the weight gain; ^d composition corresponds to the most intense peak in the mass spectrum; ^e lattice parameter b is equal to $37.97(8) \text{ \AA}$.

It was found⁴⁶ that at room temperature, $C_{60}F_{48}$ has a body-centred tetragonal cell with the parameters $a = 11.852(8)$ and $c = 17.91(1)$ Å. It was assumed previously⁵³ that the $C_{60}F_{48}$ structure can be described by an orthorhombic cell (see Table 6). Comparison of X-ray diffraction data for fluorofullerene samples with different molecular compositions (Fig. 10) shows that, where a mixture of fluorofullerenes with averaged composition is concerned, the crystal structure corresponds to an FCC lattice similar to that of C_{60} , whereas the $C_{60}F_{48}$ fullerene has a body-centred tetragonal lattice.

4. NMR spectroscopy

^{19}F NMR of solutions. The NMR method was first employed to study the products of fullerene fluorination back in 1991.¹⁷ The ^{19}F NMR spectra of solutions of fluorofullerenes in acetone or tetrahydrofuran exhibit singlet peaks with chemical shifts of -150.5 and -152.7 ppm. It was suggested¹⁷ that either one or both peaks were due to the $C_{60}F_{60}$ molecule in which all fluorine atoms are equivalent. However, the mass spectra of these samples did not show the presence of $C_{60}F_{60}$.

Some ^{19}F NMR spectra had a signal at -188 ppm, due to the hydrogen fluoride resulting from the reactions of fluorides with the residual water in acetone.¹⁷ It has been found⁵⁴ that the integral intensity of the ^{19}F NMR signal of the fluoride ion in THF depends on the amount of water in THF.

Kniaz *et al.*¹⁹ have employed the ^{19}F NMR method to study acetone solutions of the product of fluorination of C_{60} , the product of its sublimation at 300 °C and the non-volatile residue after sublimation. The ^{19}F NMR spectra thus obtained were identical to those reported in the study cited above.¹⁷ Analysis of the initial fluorofullerene by mass spectroscopy showed that the intensity of the peak due to the $C_{60}F_{60}$ molecule was 10^5 times lower than that of the most intense peak, which corresponded to the $C_{60}F_{40}$ molecule. After sublimation, the mass spectra of neither the sublimate nor the residue exhibited signals for $C_{60}F_n$, where $n \geq 50$. The researchers explained this outcome by assuming that less stable, higher fluorofullerenes were destroyed during sublimation to give F_2 or CF_4 . It was found that the NMR signal intensity passes through a maximum (corresponding to the composition $C_{60}F_{36}$) as fullerene gets saturated with fluorine. Hence, the signal at -149 ppm could belong to yet another highly symmetrical molecule, $C_{60}F_{36}$.

The ^{19}F NMR spectrum of a THF solution of fluorofullerene (prepared¹⁷ by direct fluorination of C_{60}) studied by Boltalina *et al.*⁵⁵ looked like those reported previously.^{17, 19, 54} Unlike earlier studies, in this study, the solution was analysed by mass spectroscopy. The spectra contained intense peaks in the region of small masses (which were not identified) but no signals corresponding to fluorofullerenes. This outcome may be due to the chemical interaction of fluorofullerene with the solvent; this would account for the fact that the data obtained by NMR spectroscopy for solutions of fluorofullerenes in THF or acetone do not agree with the data obtained by other methods which do not require dissolution of samples.

The line occurring at ~ -150 ppm in the ^{19}F NMR spectrum of a THF or acetone solution of fluorofullerenes can apparently be attributed to the product of decomposition of fluorofullerenes accompanied not only by the loss of fluorine but also by destruction of the carbon skeleton. The composition of the products of reactions between THF or acetone and fluorofullerenes $C_{60}F_x$ has not yet been identified. To eliminate the influence of solvents, NMR studies of solid samples should be carried out.

^{19}F NMR of solid samples. Static ^{19}F NMR spectra of solid $C_{60}F_n$ fluorofullerenes have been reported.^{24, 25} The spectra consist of one broad line with $\delta -153$ ppm and the half-width $\Delta\nu_{1/2} = 60-120$ ppm (Fig. 11). The δ values observed in the NMR spectra of a black sample (the mass spectrum of which exhibited ions corresponding to C_{60} , C_{70} and low-fluorine fluorofullerenes) and of a pale-yellow sample consisting mainly of fluorofullerenes were identical. The NMR spectra differed only in

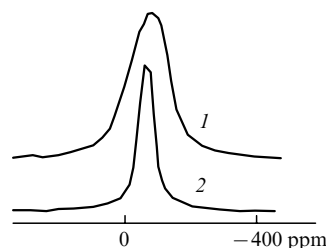


Figure 11. ^{19}F NMR spectrum (relative to CF_3CO_2H) of solid samples of $C_{60}F_n$ fluorofullerenes at 20 (1) and 300 °C (2).^{35, 36}

the $\Delta\nu_{1/2}$ value, which was 115 ppm for the pale-yellow sample and 140 ppm for the black one. Fluorination of C_{60} with molecular fluorine for two weeks at room temperature gave a light-brown fluorofullerene, which was then sublimed at 150 °C. The ^{19}F NMR spectrum of this sample exhibited a narrow peak at -155 ppm with $\Delta\nu_{1/2} = 8$ ppm. It was suggested²⁵ that this peak width corresponded to highly symmetrical molecules such as $C_{60}F_{60}$ or $C_{60}F_{36}$. The spectra of some fluorofullerene samples sublimed at 110 °C and 150 °C had an additional signal with $\delta = -133$ ppm; this was attributed to the presence of oxyfluorides $C_{60}F_{60-2y}O_y$. Unfortunately, the researchers did not investigate the composition of the samples; therefore, the reliability of the conclusions drawn cannot be judged.

^{13}C NMR. A solid sample having $C_{60}F_{46}$ as the major component (according to the data of mass spectroscopy) was studied by ^{13}C NMR.⁴¹ The technique of $^{13}C-^{19}F$ polarisation exchange showed that the sample was a mixture of compounds differing from one another in molecular motion parameters. For one of the components characterised by fast molecular re-orientations (similar to those observed in plastic crystals), the ratio of the $sp^2:sp^3$ resonance lines was found to be $14:46$, *i.e.* it complied with the stoichiometry $C_{60}F_{46}$, determined from the mass spectroscopy data. The resonance lines of the sp^2 -hybridised carbon atoms occurred in the region of $140.0-142.5$ ppm, while those of sp^3 carbon were manifested at $86-90$ ppm. However, in addition to the lines assigned to $C_{60}F_{46}$, the ^{13}C NMR spectrum exhibited a broad band at 118 ppm having $\Delta\nu_{1/2} = 40$ ppm and an intensity of $20 \pm 10\%$ of the total peak intensity. The dynamics of cross-polarisation of this line indicated that the other component of the sample comprises molecules immobile in the solid phase.

5. Molecular structure of $C_{60}F_{48}$

Experimental data on the structure of $C_{60}F_{48}$ were first obtained by Gakh *et al.*³⁰ Mass-spectroscopic analysis of the specimen they studied (the procedure of the synthesis is described in Section II.3) showed that the intensity of the ion derived from the $C_{60}F_{48}$ molecule amounted to 69% of the total intensity of ions derived from $C_{60}F_{2n}$ ($2n \leq 48$). The ^{19}F NMR spectrum of a solution of this sample in the $CFCl_3-CDCl_3$ mixture exhibited eight main lines with equal intensities (Fig. 12). It was found³⁰ that this spectrum can be attributed to 14 isomers of $C_{60}F_{48}$ including optical isomers which contain eight groups of equivalent fluorine atoms. Using ^{19}F (COSY) homonuclear correlation spectroscopy, a two-dimensional spectrum of $C_{60}F_{48}$ was recorded,³⁰ in which the cross-peaks were due to the spin-spin scalar interactions of the fluorine nuclei in the system. Based on this spectrum, the molecular structure of the fluorofullerene shown in Fig. 13a was proposed. The use of homonuclear two-dimensional $^{19}F-^{19}F$ COSY spectroscopy for $C_{60}F_{48}$ ³¹ revealed additional cross-peaks, which were consistent with the proposed structure.³⁰ Note that Boltalina *et al.*³¹ fluorinated a fullerene extract ($C_{60}:C_{70} = 3:1$) and, according to mass spectrometry, the fluorination product contained up to 30% of $C_{70}F_x$ ($x = 44-56$) and traces of fluorinated higher fullerenes ($C_{76}F_y$ and $C_{84}F_z$). However, these impurities barely influenced the NMR spectral pattern.

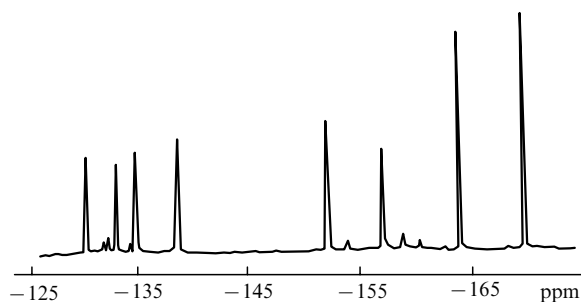


Figure 12. ^{19}F NMR spectrum of a solution of $\text{C}_{60}\text{F}_{48}$ in the $\text{CFCl}_3\text{--CDCl}_3$ system.³⁰

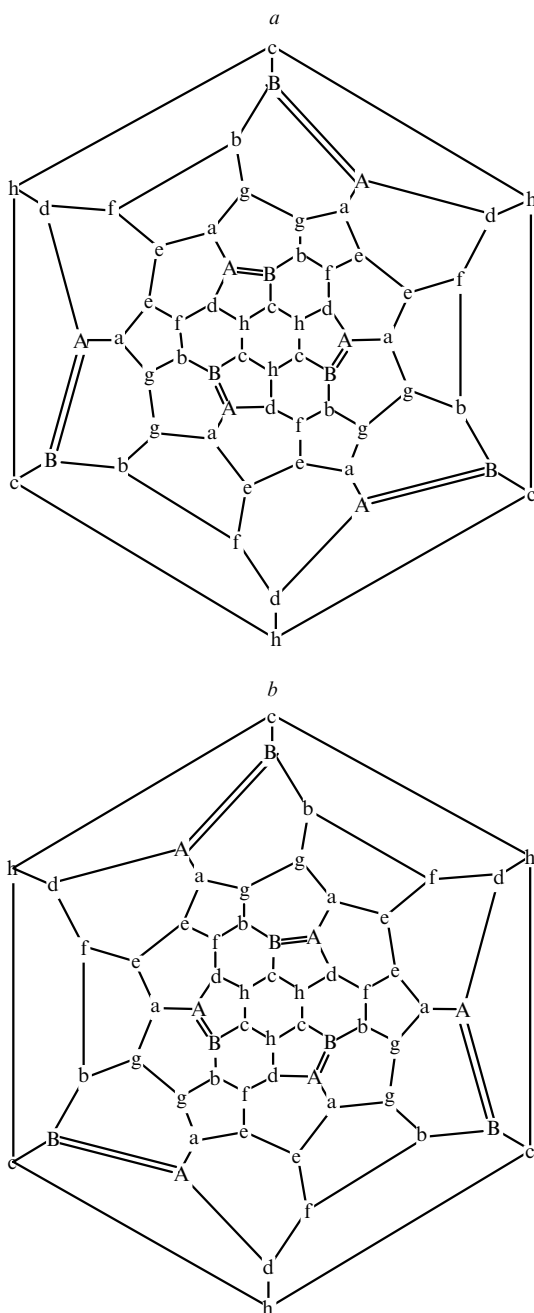


Figure 13. Schlegel diagrams for optical isomers of the $\text{C}_{60}\text{F}_{48}$ molecule with D_3 symmetry (a)³⁰ and with S_6 symmetry (b).^{35,36} The atoms equivalent in symmetry are denoted by the same characters, (a–f) for F atoms and A and B for C atoms.

Semi-empirical quantum-mechanical calculations for the relative stability of nine isomers of $\text{C}_{60}\text{F}_{48}$, namely, five chiral pairs with D_3 symmetry and four meso forms with S_6 symmetry, have shown³⁵ that two of these isomers, namely, those presented in Fig. 13, are more stable than any other isomer by at least 175 kJ mol^{-1} . In addition, the difference between the energies of formation of these isomers is negligibly small and amounts to 2 kJ mol^{-1} . In view of the size of the molecular system in question and the degree of uncertainty inherent in semi-empirical methods, these isomers can be regarded isoenergetic. The double bonds in them are located only at the edges shared by pentagons and hexagons in the carbon cage (see Fig. 13). The presence of a double bond at an edge shared by two hexagons increases the energy of formation of $\text{C}_{60}\text{F}_{48}$ by 174.7 kJ mol^{-1} . Conjugation of double bonds is a destabilising factor, which increases the $\Delta_f H$ value by 500 kJ mol^{-1} with respect to that of the most stable isomer.

Since the shape of fluorofullerene molecules is nearly spherical, it would be natural to expect molecular mobility in the crystalline phase similar to that observed for C_{60} fullerene.¹⁰ Figure 14 presents the variation of the static ^{19}F NMR spectra of fluorofullerenes vs. temperature. These data (Fig. 14a) indicate that, as the temperature decreases to 320 K and below, the velocity of re-orientation of the $\text{C}_{60}\text{F}_{48}$ molecules in the fluorofullerene crystal lattice smoothly decreases, and at temperatures below 260 K, the rotational re-orientation of molecules stops on the NMR time scale, the spectrum exhibiting one broad line with $\Delta\nu_{1/2} = 40\,000\text{ Hz}$. At temperatures above 320 K, the $\text{C}_{60}\text{F}_{48}$ molecules rotate isotropically, the velocity of rotation being sufficient for observing the fine structure in the signals of the two groups of fluorine atoms in fluorofullerene molecules.⁵⁶

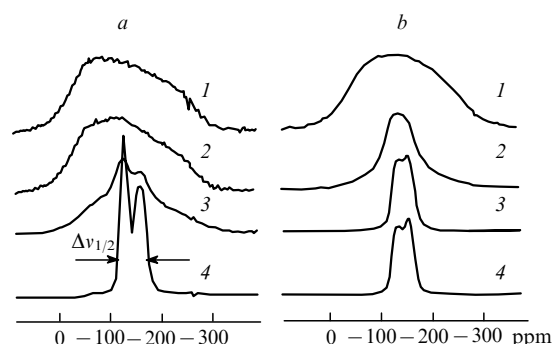


Figure 14. Variation of the static ^{19}F NMR spectrum of crystalline $\text{C}_{60}\text{F}_{48}$ (a) and $\text{C}_{60}\text{F}_{46}$ (b) fluorofullerenes as a function of temperature /K: (1) 200, (2) 260, (3) 300, (4) 340.

The high-resolution ^{19}F NMR spectrum of a polycrystalline sample of $\text{C}_{60}\text{F}_{48}$ consists of eight lines with equal intensities, which correspond to eight groups of magnetically non-equivalent fluorine atoms in the $\text{C}_{60}\text{F}_{48}$ molecule. It should be noted that the chemical shifts of these lines⁵⁶ virtually coincide with the chemical shifts observed in the ^{19}F NMR spectrum recorded for a solution of $\text{C}_{60}\text{F}_{48}$ in CDCl_3 .³⁰ Thus, the crystal lattice does not exert significant influence, compared to the influence of the solvent, on the ^{19}F chemical shifts of $\text{C}_{60}\text{F}_{48}$. The four groups of low-intensity lines ($< 10\%$ of the total intensity of peaks) observed in the spectra of both solutions and solid samples can apparently be assigned to $\text{C}_{60}\text{F}_{2n}$ impurities ($2n < 48$) or to other $\text{C}_{60}\text{F}_{48}$ isomers.

The high-resolution ^{13}C NMR spectra of a $\text{C}_{60}\text{F}_{48}$ sample exhibit two equally intense lines in the region of signals corresponding to sp^2 carbon atoms, pointing to the presence in the $\text{C}_{60}\text{F}_{48}$ molecule of two magnetically non-equivalent groups of carbon atoms not attached to fluorine atoms.⁵⁶ In accordance with the ^{19}F NMR spectrum, the region of signals of the sp^3

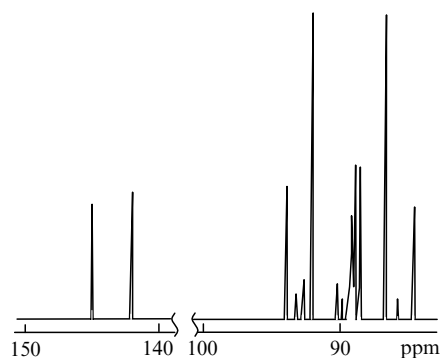


Figure 15. ^{13}C NMR $\{^1\text{H}, ^{19}\text{F}\}$ spectrum of a solution of $\text{C}_{60}\text{F}_{48}$ in CDCl_3 (recorded by Prof. T Ono, Japan).

carbon nuclei should contain eight peaks corresponding to eight magnetically nonequivalent groups of carbon atoms attached to fluorine atoms. However, the spectral pattern was fairly complex because each of the eight expected lines was split due to the scalar ^{13}C – ^{19}F spin–spin interaction. The complex multiplet was resolved by using equipment for C–F decoupling (Fig. 15). It is worth noting that ^{13}C NMR data obtained by other investigators⁴¹ only pointed out the presence of non-resolved broad bands in the regions of sp^2 and sp^3 carbon signals.

Thus, the compound $\text{C}_{60}\text{F}_{48}$ has been studied comprehensively by NMR spectroscopy; it was found that the isomeric purity of this compound prepared by direct fluorination of C_{60} reaches 90%, which is a startling result if one recalls that tens of thousands geometrical isomers of $\text{C}_{60}\text{F}_{48}$ can theoretically exist. To elucidate the molecular structure more precisely (to choose between the most probable structures, D_3 and S_6), experimental and theoretical data of IR and Raman spectroscopy and crystallography should be resorted to. Additional experiments are needed including the synthesis of $\text{C}_{60}\text{F}_{48}$ with an endohedral ^3He atom and subsequent analysis of the chemical shifts in the ^3He NMR spectra.

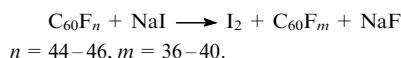
IV. Chemical properties of fluorofullerenes

Fluorocarbon polymers such as Teflon are known to be exceptionally chemically inert, being able to react slowly only with liquid sodium metal. This is due to the great strength of the C–F bond (460 – 540 kJ mol^{-1}), the non-polar character of this bond and the rigidity of carbon chains covered by a shell of fluorine atoms. A similar type of behaviour could have been expected of fluorofullerenes. However, fluorofullerenes were found to exhibit oxidative properties. A typical feature of fluorinated fullerene derivatives is high reactivity. Strong repulsion of fluorine atoms from one another is supposed to be the driving force of reactions. The C–F bond length in fluorofullerenes is 1.49 Å;²³ for comparison, this bond length in aliphatic fluorocarbons is 1.38 Å.⁴ Correspondingly, the energy of the C–F bond in fluorofullerenes is 150 – 250 kJ mol^{-1} lower than that in aliphatic fluorocarbons. According to both kinetic and thermodynamic factors, fluorofullerenes have lost the inertness of the C–F bond, typical of fluorocarbons; fluorine can be transferred to electron-saturated compounds and electrons can be captured from some reagents such as benzene.

The chemical properties of fluorofullerenes have been poorly studied yet. This is due to several reasons, namely, inaccessibility of macroscopic quantities of the compounds and the difficulty of the analysis of the reaction products (*i.e.* the formation of mixtures of compounds with closely similar properties).

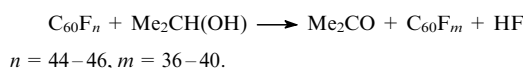
It has been reported⁵⁷ that highly fluorinated fluorofullerenes enter into a number of oxidative reactions (with sodium iodide or isopropanol) and into fluorination reactions (with aromatic compounds in the presence of Lewis acids). Mixing a solution of a

$\text{C}_{60}\text{F}_{44}$ – $\text{C}_{60}\text{F}_{46}$ fluorofullerene mixture with 0.1 M NaI in acetone results in immediate evolution of iodine; after keeping the mixture for several hours at room temperature, a black precipitate is formed. Analysis of the reaction solution by mass spectroscopy shows the presence of fluorofullerenes with a fluorine content lower than that in the initial sample.

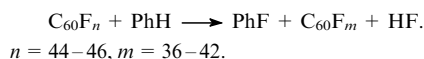


It was shown that fluorofullerenes react with bromides in a similar way. In the reaction with tetrabutylammonium bromide in chloroform, immediate evolution of bromine was observed.

The reaction with isopropanol proceeding on prolonged heating (85°C) afforded 1.6 moles of acetone per mole of fluorofullerene.



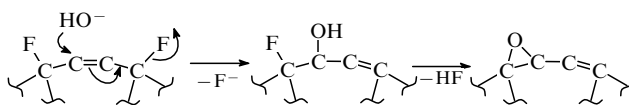
The reaction of fluorofullerenes with benzene in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ was studied. Mass-spectroscopic analysis of the reaction mixture, the colour of which slowly changed from yellow to brown, indicated the formation of fluorobenzene and the presence of fluorofullerenes with lower mass numbers. It was noted that degradation of fluorofullerenes C_{60}F_x is accelerated as x increases. Some reactions result in the formation of a black resin.



It should be noted that even pyridine, which is well known to be inert towards electrophilic substitution, does react slowly with higher fluorofullerenes at elevated temperatures giving rise to 2-fluoropyridine (the yield reaches 10%).

Unfortunately, it cannot be understood from the results obtained what is the mechanism of these reactions, whether it is ionic (fluorine transfer) or radical (electron transfer). On the one hand, the predominant formation of biphenyl in the reaction of fluorofullerene with phenyllithium supports the radical mechanism, while, on the other hand, fluorination of pyridine is a typical ionic process (by analogy with the well known reactions of pyridine with other electrophilic fluorinating agents).

In one of the first publications dealing with fullerene fluorination,⁵⁸ it was noted that fluorination products tend to enter into a nucleophilic substitution reaction, namely, the OH^- anion reacts with a double bond in fluorofullerene, then HF is eliminated and fluorofullerene oxide is produced.



As noted above, detailed investigation of the chemical properties of fluorofullerenes is possible only provided that individual compounds are available and their molecular structures and the degrees of purity are known. In the last two years, certain progress has been attained along this line. In particular, the isolation of pure $\text{C}_{60}\text{F}_{18}$ and of its oxo derivative $\text{C}_{60}\text{F}_{18}\text{O}$ are worthy of note.^{59,60} An example of chemical transformation of individual fluorofullerenes is the reaction of $\text{C}_{60}\text{F}_{18}$ with benzene in the presence of FeCl_3 , known as the Friedel–Crafts reaction, which resulted in the synthesis of $\text{C}_{60}\text{F}_{15}\text{Ph}_3$, called ‘triumphene’.⁶¹

V. Thermodynamic studies of the fluorofullerene $\text{C}_{60}\text{F}_{48}$

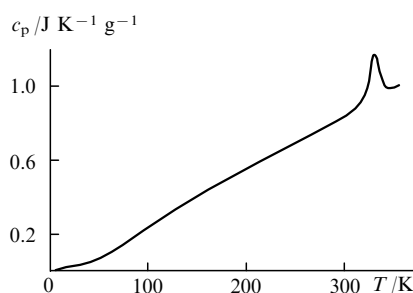
The thermodynamic properties of $\text{C}_{60}\text{F}_{48}$ known to date are summarised in Table 7.

The low-temperature heat capacity of $\text{C}_{60}\text{F}_{48}$ in the temperature range from 8 to 356 K was measured by adiabatic calorimetry.^{62,65} These data were used to calculate the numerical values of

Table 7. Thermodynamic characteristics of C₆₀F₄₈.

Characteristic	Value	Ref.
$C_{p,m}(298.15) / \text{J K}^{-1} \text{mol}^{-1}$	1365.2 ± 2.7	62
$H_m^\circ(298.15) - H_m^\circ(0) / \text{kJ mol}^{-1}$	192.48 ± 0.83	62
$S_m^\circ(298.15) - S_m^\circ(0) / \text{J K}^{-1} \text{mol}^{-1}$	1137.2 ± 5.7	62
$G_m^\circ(298.15) - H_m^\circ(0) / \text{kJ mol}^{-1}$	146.6 ± 2.9	62
$\Delta_f S_m^\circ(298.15) / \text{J K}^{-1} \text{mol}^{-1}$	-4071.6 ± 5.8	62
$\Delta_s H_m^\circ(476) / \text{kJ mol}^{-1}$	109 ± 7	63
$\Delta_f H_m^\circ(\text{cryst.}) / \text{kJ mol}^{-1}$	-7563 ± 166	64
$\Delta_f H_m^\circ(\text{gas}) / \text{kJ mol}^{-1}$	-7454 ± 166	64

the thermodynamic functions $H^\circ(T) - H^\circ(0)$, $S^\circ(T) - S^\circ(0)$ and $G^\circ(T) - H^\circ(0)$. The curve for the variation of the specific heat capacity of C₆₀F₄₈ as a function of temperature, presented in Fig. 16 displays a phase transition in the temperature range of 315–345 K ($T_{tr} = 329.6 \pm 0.4$ K and $\Delta_{tr}H = 7.0 \pm 0.7$ kJ mol⁻¹). According to NMR and X-ray diffraction data, this transition is due to the transformation of the ordered body-centred tetragonal phase into a face-centred cubic plastic phase.

**Figure 16.** Specific heat capacity of C₆₀F₄₈ vs. temperature.⁵⁶

The partial pressures of C₆₀F₄₈ have been measured in the temperature range of 395–557 K by high-temperature mass spectroscopy using PbI₂ and C₆₀F₃₆ as internal standards.⁶³ The researchers suggested calculating the partial pressures (in Pa) using the equation

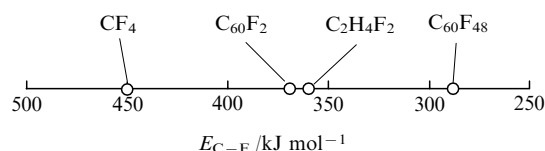
$$\ln[p(\text{C}_{60}\text{F}_{48})] = -\frac{13\,146}{T} + 24.34.$$

The enthalpy of sublimation of C₆₀F₄₈ (see Table 7) calculated using the second law of thermodynamics is lower by 66 kJ mol⁻¹ than the enthalpy of sublimation of C₆₀ (175 ± 3 kJ mol⁻¹), which is due to the smaller energy of intermolecular interactions in the fluorofullerene.

The energy of combustion of C₆₀F₄₈ for burning in a rotating bomb calorimeter ($-24\,638 \pm 163$ kJ mol⁻¹) and the standard molar enthalpy of formation of C₆₀F₄₈ in the crystalline state have been determined⁶⁴ (see Table 7).

In 1992, the $\Delta_f H_m^\circ(\text{gas})$ values for C₆₀F₄₈ were estimated by semi-empirical MNDO and AM1 methods.⁶⁶ The values found for C₆₀F₄₈ isomers formed upon the addition of fluorine atoms to C₆₀ with and without rupture of the C–C bonds in the carbon cage were -7395 and -5508 kJ mol⁻¹, respectively. The former value is close to the enthalpy of formation found experimentally; however, in view of the molecular structure of fluorofullerene C₆₀F₄₈ now established (see Section IV), which rules out the presence of =CF₂ groups in the molecule, this appears to be an accidental coincidence.

The energy of the C–F bond in C₆₀F₄₈ calculated from experimental data⁶⁴ proved to be 36% lower than that in CF₄ (Fig. 17). The reason is elongation of the C–F bonds in C₆₀F₄₈ with respect to those in tetrafluoromethane, difluoroethane or difluorofullerene due to steric factors.

**Figure 17.** Energy of the C–F bond in some fluorocarbons.

VI. Conclusion

In conclusion, we would like to mention some lines of investigation into direct fluorination of fullerenes which appeared recently and are, in our opinion, the most interesting and promising. In the near future, the search for the routes of the selective synthesis of fluorofullerenes, especially those with low fluorine contents (less than 36 fluorine atoms per fullerene molecule) would be continued. As shown above, no convincing evidence supporting the assumption that low-fluorine compounds can form in substantial amounts in the reaction of F₂ with fullerene can be found in the literature. Indirect data indicate that these compounds could be prepared by liquid-phase fluorination; however, exhaustive spectroscopic investigation of the reaction products is still to be performed.

Recent studies of Chilingarov *et al.*^{28,67} in which fullerene mixed with transition metal difluorides is treated with molecular fluorine at elevated temperatures deserve attention. The use of transition metal difluorides as catalysts restricts substantially both the number of the products formed and the degree of saturation of fullerene molecules with fluorine. Nevertheless, it is still unclear whether this method would prove more efficient than the known solid-phase reactions involving trifluorides of metals of the first transition row.

Development of methods for purification and separation of fluorination products would remain among the most topical tasks. Attempts of using various methods for the separation of fluorofullerene mixtures resulting from direct fluorination have been reported in the literature. In particular, a technique used fairly often for this purpose is sublimation. However, these attempts have not yet been a success because the properties of compounds with close contents of fluorine (36 to 48 fluorine atoms per fullerene molecule) are close. Nevertheless, a series of recent publications dealing with chromatographic separation of several fluorofullerenes, their oxidised forms and even fluorofullerene isomers prepared by reactions with metal fluorides demonstrated high efficiency of this method as applied to the given class of compound.^{68,69} The most impressive example is isolation of > 40 individual compounds from a C₇₀F_x sample prepared by the reaction of C₇₀ with MnF₃. Among these 40 compounds, seven isomers of C₇₀F₃₆ alone were present.⁷⁰

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The formation of carbon filaments upon decomposition of hydrocarbons catalysed by iron subgroup metals and their alloys

V V Chesnokov, R A Buyanov

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Abstract. The structure of filamentous carbon formed upon catalytic decomposition of hydrocarbons on iron subgroup metals and their alloys is considered. The regularities of the deposition of carbon on these metals are generalised. The carbide cycle mechanism of carbon formation is considered in detail. The growth models of some morphological modifications of filamentous carbon are discussed. The bibliography includes 151 references.

I. Introduction

Deactivation of catalysts may be determined by a number of factors,¹ one of which is carbonisation (coking) of catalysts in the processing of hydrocarbons. The development of an efficient method for combating this phenomenon would allow substantial extension of the lifetime of catalysts; therefore, the interest of investigators in the mechanisms of catalytic formation of carbon has not decreased for many decades. This interest is also due to the fact that in a number of cases, the carbonised mineral phases (metals, oxides, and others) and carbon itself can be regarded as carbon-mineral and carbon composite materials possessing special properties.

The formation of filamentous carbon upon decomposition of hydrocarbons on iron subgroup metals and their alloys is one of the most exotic (from the viewpoint of its mechanism) and practically important processes. The properties of carbon graphite deposits on catalysts are mainly determined by their morphological and crystallographic features. The main task in the development of technologies for the preparation of a broad spectrum of such composites should be the elaboration of a scientifically substantiated procedure of process control. To the end, it is necessary to know the mechanisms underlying all its stages.

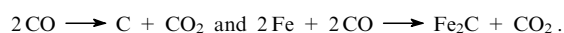
II. The carbide cycle mechanism of carbon formation

1. Decomposition of hydrocarbons on metallic iron

Various suggestions on the possible role of carbides as intermediates in the formation of carbon deposits were put forward in early

studies generalised by Storch *et al.*² in their monograph nearly five decades ago. It has been noted, in particular, that the hypothesis according to which carbides are intermediates in the formation of free carbon is attractive but stands in need of evidence.

Kagan *et al.*³ considered carbonisation of an iron catalyst to be the result of two independent reactions



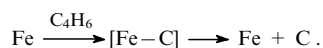
However, a later study proved⁴ that the important parts of the process of carbon formation in the decomposition of hydrocarbons on iron are the steps of carbide formation and decomposition.

The proposed carbide mechanism of carbon formation could be confirmed by the establishment of a common limiting step and a common intermediate in the formation of a carbide and carbon. To this end, the activation energies of carbon and iron carbide formation^{5,6} were measured in the experiments on carbonisation of iron in the butadiene decomposition. The formation of the carbide in the temperature range 573–723 K is virtually unaccompanied by its decomposition and liberation of carbon. The formation of iron carbide Fe_3C is a topochemical reaction, *i.e.*, it occurs through formation and growth of nuclei of the carbide phase. An integral kinetic curve of the reaction is S-shaped; therefore, an approximate formula⁷ is used to determine the specific rate of carbidisation

$$W = 2 \frac{W_{\max}}{\pi S},$$

where $W_{\max}$ is the maximum observed rate of carbidisation, S is the specific surface of a sample. The activation energy was determined from the $W_{\max}$ values at different temperatures.

In the range of temperatures 808–874 K, the activation energy of carbide decomposition (197 kJ mol^{-1}) is substantially higher than that of its formation (88 kJ mol^{-1}). For this reason, the ratio between the rates of these reactions changes with temperature. Above 1023 K, the rate of iron carbide decomposition exceeds the rate of its formation, and the carbide phase is not formed. Investigations into the kinetics of carbon formation on iron showed that the activation energy of carbon formation at 1023–1027 K amounts to 96 kJ mol^{-1} and becomes close to that of carbide formation. Obviously, the common limiting step of both reactions is the formation of an intermediate, surface carbide-like compound of the type $[\text{Fe}-\text{C}]$. This makes it possible to represent the mechanism of formation of carbon deposits on iron with the following scheme:



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In our studies, this mechanism has been called the carbide cycle mechanism.^{4–6,8–17} The reactions proceed in an open flow system from which the gaseous decomposition products are removed; therefore, the thermodynamic restrictions here are of minor significance.

The carbide cycle mechanism includes two basic steps:⁵ the ‘chemical’ step in which the catalytic decomposition of hydrocarbons occurs on the surface of a metal particle with the formation of carbon atoms whose concentration increases to definite limiting values, and the ‘physical’ step in which the crystallisation centres (nuclei) of the graphite phase are formed on definite faces of a metal particle. In this step, migration (diffusion in the bulk of the metal particle) of carbon atoms towards these centres and growth of a definite variety of graphite particles, predominantly in the form of filaments begin.

Despite the fact that the formation of carbon comprises two steps, the mechanism, on the whole, was called the mechanism of the carbide cycle since the carbon atoms involved in the graphite formation ‘originate’ from intermediate carbide compounds.

The character of carbon deposits is determined by the properties of metal catalyst particles, the nature of a hydrocarbon, as well as by the distinctive features of crystallisation centres and mass-transfer of carbon atoms.

The mechanism of the carbide cycle considered above in the example of the model system $\text{Fe} + \text{C}_4\text{H}_6$ can also be extended to the decomposition of other hydrocarbons. Naturally, the activation energies of formation of carbon deposits from different hydrocarbons differ substantially: *e.g.*, for methane, butane, propylene, isobutylene and butadiene they are ^{6,18} 209, 184, 146, 138 and 96 kJ mol^{-1} , respectively. The relationship between the activation energies (E_a) and enthalpies (ΔH) of the iron carbide formation from different hydrocarbons (Fig. 1) is described by the Brönsted–Polanyi equation.

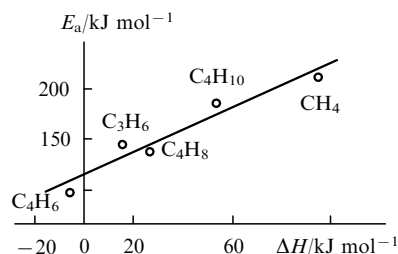
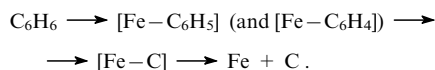


Figure 1. Dependence of the activation energy of carbon formation on the enthalpy of iron carbide formation in the decomposition of various hydrocarbons.

The formation of carbon from aromatic hydrocarbons can also occur by the carbide cycle mechanism. This was demonstrated in the example of benzene decomposition on metallic iron.¹⁹ At temperatures above 773 K, the catalyst in the steady state is in the form of metal, whereas below this temperature the metallic iron passes to the carbide. The formation of carbon from benzene on metallic iron in the temperature range 773–998 K can be described by the scheme



At temperatures above ~ 898 K, the limiting step is the dissociative adsorption of benzene accompanied by the formation of C_6H_5 or C_6H_4 species,^{20–22} while below this temperature the reaction is limited by the scission of the benzene ring with the formation of intermediate carbide-like compounds.

2. The role of topochemical processes in the mass-transfer of carbon in the carbide cycle mechanism

Studies of the carbon phase formation on metallic iron suggest the elucidation of not only the mechanism of decomposition of hydrocarbons with liberation of carbon atoms, but also of the mode of generation and formation of a new phase from these atoms. The theory of solid-phase reactions²³ and the theory of crystallisation²⁴ are based on the assumption that the initial formation of nuclei of a new phase is often the limiting step of these processes. Under the conditions of topochemical process, the nuclei are formed on the active centres the role of which can be played by surface defects, associates, clusters, sites of the exit of dislocations onto the surface of crystals, *etc.*

In the decomposition of hydrocarbons accompanied by the formation of intermediate carbide-like compounds, carbon atoms are liberated which diffuse into the bulk of the metal and form there a solid solution.¹³ The question arises of how the nuclei of the new phase (graphite) are formed and how does the transport of carbon to these nuclei occur.

In accordance with the carbide cycle mechanism,^{4–6,10–18,25} the subsurface layer of the metal becomes supersaturated (by over two orders of magnitude) with the carbon liberated in the decomposition of intermediate carbide compounds. Indeed, the decomposition of intermediate carbide compounds forms a mixture of carbon and the metal in which the C:Fe ratio appears to correspond to the composition Fe_3C (~ 6 mass % – 7 mass % of carbon), whereas the saturated solution of carbon in iron contains not more than 0.025 mass % of carbon.²⁶ The concentration of carbon is averaged over the bulk of the metal, and this results in the appearance of a graphite nucleus at one of the sites of the metal particle surface. The growth of the graphite phase occurs by virtue of excess carbon in the supersaturated solution. High gradients of carbon concentration appear between the surface site where decomposition of hydrocarbons takes place and the site where the graphite phase is formed. The presence of such a gradient ensures the diffusive transport of carbon atoms through the bulk of a metal particle.

The appearance of a concentration gradient in a solution of carbon in the metal is explained by the specific features of carbon formation through the carbide cycle mechanism and by the difficulties of graphite nuclei formation.

The above considerations make it possible to present a general scheme of all the steps of the graphite phase formation. The activation energies of deposition of carbon formed upon decomposition of acetylene on α -iron (E_c) and diffusion of carbon through the α -iron phase (E_d) are close,²⁷ their values are within the range 67–80 kJ mol^{-1} . This is only possible provided the activation energy of decomposition of hydrocarbons by the carbide cycle mechanism (E') is smaller than E_d . In this case, the growth of the carbon phase is limited by the step of diffusive transfer of carbon, which predetermines the apparent equality $E_c \simeq E_d$. However, the activation energy of the decomposition of a number of more stable hydrocarbons by the carbide cycle mechanism may be rather high and $E' > E_d$; in this case it is not the carbon diffusion but rather the formation of intermediate compound $[\text{Fe}-\text{C}]$, *i.e.*, decomposition of hydrocarbons, that becomes the limiting step. Then the values of E' and E_c coincide. Thus, the diffusion of carbon in the metal from the site of its liberation towards the nucleus or the graphite phase on which it condenses is an important step in the catalytic process of carbon deposition on metals.¹³ Deposition of carbon on iron subgroup metals occurs at increased temperatures when carbides of these metals are not formed (for Fe, Ni and Co, these temperatures amount to 1023, 673 and 573 K, respectively).

Relevant experiments have shown²⁸ that the formation of graphite nuclei is a more energy-consuming process than the carbide phase formation. This may be explained by the fact that

carbon is formed by the carbide cycle mechanisms through an intermediate surface carbide compound which is transformed into carbide after saturation with carbon from its solid solution in the metal.¹³ Under definite conditions, the deposition of carbon can begin with the formation of a thermodynamically unstable metastable carbide phase.²⁹⁻³² The carbide formation accompanied by the liberation of elementary carbon was observed, in particular, in CO disproportionation on iron.⁷ In this case, the accumulation of carbon in the carbide phase may be regarded as only an intermediate step in the formation of graphite nuclei. Owing to this step, the concentration of carbon in the metal bulk may be considerably higher than merely in the saturated solution of carbon in the metal.

3. The formation of carbon on iron carbide

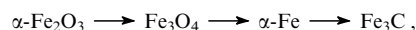
As noted above, under definite conditions a metal catalyst undergoes some changes under the action of the reaction medium and can exist in the form of a metastable carbide in the steady state. For this reason, irrespective of whether the metal or the carbide is the active origin of the process of carbon formation, one can say that carbon will be formed by the carbide cycle mechanism.

Accumulation of carbide-like compounds leads first to the appearance of the Fe_3C phase nuclei and then to the complete phase transformation of the metal into the carbide. The carbide mechanism of the formation of carbon deposits on Fe_3C is preserved in any case; however, the features of its implementation are determined by the chemical nature of the active phase.

The chemical nature of the active phase is primarily manifested in the step of decomposition of an intermediate carbide-like compound. The limiting step of the formation of carbon deposits on the metal is the formation of a carbide-like compound, whereas its decomposition and aggregation of the liberated carbon atoms occur rather quickly. The limiting step of carbon formation on the carbide is the liberation of carbon atoms from the carbide, the carbide passing to a transient state with a disturbed stoichiometry. The disturbed stoichiometry of the surface carbide is recovered upon hydrocarbon decomposition. As the bulk of a catalyst contains a considerable amount of carbon, the diffusive transfer of carbon atoms through the carbide bulk virtually does not take place, while their surface migration is negligible. In this case, the carbon phase is formed as islets or a continuous film shielding the catalyst's surface.

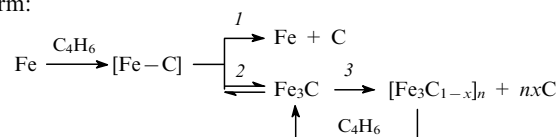
The rate of carbide decomposition increases with temperature. Direct measurements of the initial rate of Fe_3C decomposition were performed using a high-temperature X-ray chamber.^{6, 12}

It was established that $\alpha\text{-Fe}_2\text{O}_3$ undergoes various transformations under the action of the reaction medium (buta-1,3-diene diluted with helium at the molar ratio 1 : 10)



which occur over 10 min; after this the composition of the catalyst corresponds to iron carbide and remains unchanged with time. The contents of α -Fe and Fe_3C in a sample were estimated from the heights of the corresponding peaks (110) and (210) on the diffractograms. In an inert medium, iron carbide decomposes into carbon and a solid solution of carbon in α -Fe (ferrite). The initial rate of Fe_3C decomposition coincided with the rate of carbon formation in the presence of the carbide phase.⁶ This fact confirms that the formation of carbon deposits is limited by the step of carbon liberation from iron carbide. As a result, iron carbide is depleted in carbon to give a non-stoichiometric carbide with which a hydrocarbon interacts. The carbon atoms formed during decomposition of hydrocarbon by the carbide mechanism are again involved in finishing the 'build-up' of the carbide. X-Ray structural studies showed that the interplanar distances in the carbide correspond to the standard values. Consequently, in the course of reaction the system contains stoichiometric carbide Fe_3C , while the slow step is the liberation of carbon from it.

A detailed scheme of the catalytic process of formation of carbon deposits by the carbide cycle mechanism has the following form:



where $[\text{Fe}-\text{C}]$ is the carbide-like intermediate compound, $[\text{Fe}_3\text{C}_{1-x}]_n$ is the intermediate surface carbide with disturbed stoichiometry, $nx = 1$.

Depending on the conditions, either the carbide phase or the metal phase can be stable; although, naturally, only one phase exists in the steady state. The reaction route 1 corresponds to the formation of carbon from hydrocarbons on a metal without formation of the carbide phase. Reaction 2 describes the phase chemical transformations occurring under the action of the reaction medium. Reaction 3 is related to the liberation of carbon and the subsurface non-stoichiometric carbide which can be saturated with carbon under the action of gaseous hydrocarbons.

4. Specific features of the carbide cycle mechanism in the formation of carbon on nickel

The above-cited scheme of the carbide cycle describes the processes occurring on nickel, cobalt and a number of other metals. Naturally, individual features of each metal catalyst are manifested in individual steps of the formation of carbon deposits, though this takes place within the limits of the regularities described.

Let us consider, for example, the features of formation of carbon deposits from butadiene on nickel.^{6, 15}

Using a high-temperature X-ray chamber, it was shown that in the hydrocarbon medium, nickel carbide is formed at temperatures below 623 K. In this case, deposition of carbon proceeds very slowly and does not change the kinetics of carbide formation, which was therefore studied in the temperature range 548–623 K, while the kinetics of carbon formation was studied at 773–923 K. The former reaction is of first order with respect to butadiene and is characterised by an activation energy of 96 kJ mol⁻¹, while the latter is zero order and has an activation energy of 134 kJ mol⁻¹.

These distinctions indicate that the reactions of carbide formation and carbon depositions on nickel have different limit-

Table 1. Coefficients of carbon diffusion through iron subgroup metals and their temperature dependences.

T/K	Diffusion coefficient		Temperature dependence ^a	
	$D/\text{cm}^2 \text{ s}^{-1}$	Ref.	$D = D_0 \exp(-E_a/RT)$	Ref.
Iron				
773	2×10^{-8}	41	$D = 3.9 \times 10^{-3} \exp(-80.3/RT)$	43
	1×10^{-8}	43	$D = 8 \times 10^{-3} \exp(-83/RT)$	26
	2×10^{-8}	26		
873	1×10^{-7}	41		
	5×10^{-8}	43		
	8×10^{-7}	26		
Cobalt				
773	3×10^{-11}	44	$D = 0.21 \exp(-147/RT)$	44
873	5.74×10^{-10}	44		
Nickel				
773	8×10^{-11}	41	$D = 0.1 \exp(-138/RT)$	41
	2.5×10^{-11}	42	$D = 2.48 \exp(-168/RT)$	42
873	8×10^{-10}	41		
	2.5×10^{-10}	42		

^a Activation energy E_a is expressed in kJ mol^{-1} .

ing steps. The value of E_a for the second reaction is 134 kJ mol^{-1} , which corresponds to the activation energy of carbon diffusion through this metal.^{27, 33–39} Consequently, it may be presumed that the limiting step of carbon formation on metallic nickel is its diffusion through nickel to the nuclei and the graphite phase which is being formed. Thus, the limiting steps of the processes of formation of carbon deposits on iron and nickel are different. This is explained by the fact that the coefficient of carbon diffusion in α -Fe is nearly three orders of magnitude larger than that in nickel (Table 1).^{40–44}

At temperatures below 623 K, the formation of Ni_3C carbide occurs considerably faster than its decomposition; in this temperature range, carbon is formed on nickel carbide.

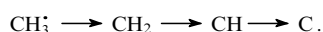
Substitution of benzene or hexane for butadiene does not affect the rate of carbon formation. This may indicate that the formation of carbon from the above-mentioned hydrocarbons on nickel is limited by the same step, *i.e.*, the diffusion of carbon atoms through the bulk of the metal.

5. Regularities of carbon formation from methane on nickel

The results of studies of the nature of the active phase of Ni/SiO_2 catalysts in the reforming of methane by carbon dioxide confirmed the important role of the surface layers of nickel carbide in both implementation of the major transformation and formation of carbon.⁴⁵ The reaction proceeds on the surface layer which is formed in the beginning of the process and which is close in its composition to nickel carbide. The adsorbed forms of carbon resulting from the activation of methane on the nickel surface are in equilibrium with methane in the gas phase. They can be irreversibly transformed to CO by reacting with adsorbed oxygen (in different forms), which results from the activation of carbon dioxide. A portion of carbon in the amount equivalent to its content in the subsurface carbide layer is rapidly dissolved in the bulk of nickel. This carbon diffuses into the bulk of the metal and is involved in the formation of carbon deposits.

Owing to high thermodynamic stability of methane, its behaviour in the process of nickel carbonisation is different from that of other hydrocarbons.

Chemisorption and subsequent decomposition of methane on the surface of nickel single crystals were studied by high-resolution spectroscopy of characteristic electron energy losses and by Auger spectroscopy.^{46–55} It was established that at lower temperatures, methane is chemisorbed in the dissociative mode with formation of the methyl radical and a hydrogen atom. On temperature increase from 373 to 600 K, the radical $\text{CH}_3^\cdot$ undergoes stepwise dehydrogenation



Schouten *et al.*⁵⁶ carried out experiments at 600 K and have proposed a similar scheme of the formation of surface nickel carbide:



Kinetic studies of methane decomposition were performed at 723–823 K in a catalytic reactor with a microbalance.^{57–59} Analysis of the results obtained was based on the model of Grabke^{60, 61} according to which the decomposition of methane on α -Fe and γ -Fe surfaces occurs as a result of successive splitting of hydrogen atoms, while the limiting step is the decomposition of the methyl radical. On the other hand, Alstrup and Tavares^{57, 59} showed that the limiting step could be both dissociative adsorption of methane and dehydrogenation of adsorbed methyl groups, whereas Snoeck *et al.*⁶² state that this process is limited by the step of detachment of the first hydrogen atom from the methane molecule adsorbed on the nickel surface.

Our kinetic studies of methane decomposition on aluminium–nickel catalysts⁶³ showed that the activation energy of carbon formation on nickel decreases as the temperature increases. In the temperature range 798–873 K, the activation energy is 75 kJ mol^{-1} , which is close to the literature data [*cf.*

88 kJ mol^{-1} (Ref. 58), 90 kJ mol^{-1} (Ref. 59), 96 kJ mol^{-1} (Ref. 64) and 97 kJ mol^{-1} (Ref. 65)]. Apparently, the limiting step is dehydrogenation of the adsorbed methyl radical with formation of surface nickel carbide, which is confirmed by the study of the kinetics of nickel carbide formation from methane on the (110) face of a nickel single crystal.⁵⁶ The activation energy of the surface nickel carbide formation is $87 \pm 12 \text{ kJ mol}^{-1}$ (see Ref. 56).

In the temperature range 923–1023 K, the activation energy of carbon formation from methane decreases to 26 kJ mol^{-1} . Similar values of the activation energy of carbon formation from methane (0 – 40 kJ mol^{-1}) were obtained for the nickel-containing catalysts,^{66, 67} as well as for the (111) and (100) faces of nickel.^{50, 51, 68} The value 26 kJ mol^{-1} coincides with the experimental E_a , which characterises the dissociative adsorption of methane on the face (100) of the nickel surface with formation of the methyl radical and a hydrogen atom.⁶⁸ This makes it possible to conclude that the limiting step of methane decomposition on nickel catalysts at 923–1023 K is the dissociative adsorption of methane with formation of a hydrogen atom and methyl radical.

III. Regularities in the formation of carbon of different morphological types on iron subgroup metals

1. Varieties of carbon deposits

Carbon formed on the iron subgroup metals or their alloys with other metals is produced in the form of deposits possessing various crystallographic characteristics, which depend on the specific features of catalysts and conditions of the process. Using these dependences, one can purposefully control the technologies of preparation of carbon deposits of various morphologies.⁶⁹ Carbon can be deposited as filaments of different configuration, nanotubes, plates and other forms.

The most interesting varieties are characteristic of the forms of filaments. Figure 2 shows three basal structures of carbon filaments.

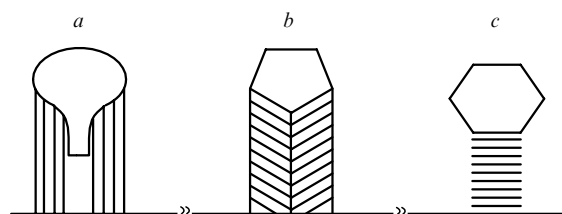


Figure 2. The structures of graphite filaments with different positions of basal planes;

(a) coaxial-cylindrical; (b) coaxial-conical; (c) flat-parallel (in the form of stacks of plates of graphite planes).

Carbon nanotubes have first been revealed as a concomitant product in the preparation of fullerenes by vaporisation of graphite in an electric arc.⁷⁰ It was shown later that nanotubes could also be obtained by catalytic methods.^{71–73} Nanotubes differ from carbon filaments primarily in their smaller sizes. Carbon nanotubes consist of 1–50 cylindrical graphite-like layers coaxially inserted into each other;^{70, 74, 75} the diameters of cylindrical cavities are 0.7–6 nm, whereas the lengths of the tubes reach several micrometers. In a chemical respect, the nanotubes obtained by graphite vaporisation differ from the known forms of carbon in their increased resistance to oxidation.⁷⁶

2. Regularities of the formation of filamentous carbon

The growth of carbon filaments is catalysed by finely dispersed metal particles. The limits of sizes were established outside which the metal particles are coated with carbon and lose their abilities

to perform catalytic functions.^{77–80} The lower limit is ~ 30 Å, while the upper limit depends on the coefficient of carbon diffusion in the bulk of the metal particle. For nickel and cobalt, these are ~ 1000 – 1500 Å. The carbon diffusion coefficient in iron is 2–3 orders of magnitude larger than that in nickel and cobalt; therefore, the upper limiting size of iron particles is at least one order of magnitude larger.⁷⁹

The growth of carbon filaments on finely dispersed particles of the iron subgroup metals and their alloys with some other metals is a physical step of the carbide cycle mechanism.^{5, 6, 9–18, 77–79} This process is to some extent unique and is of great interest for fundamental science.

The growth of carbon filaments was directly observed in the gas chamber of an electron microscope.^{33, 35} The following regularities were revealed:

(1) a particle of a catalyst is present at the growing ends of each filament;

(2) the diameter of filaments is controlled by the size of the catalytic particle at the growing end, which is fragmented in most cases, and this initiates growth of finer filaments;

(3) the diameters of filaments range from 100 to 1500 Å, while their lengths can reach 8×10^4 Å;

(4) the grown filaments have various forms (loops, helices, interwoven mass);

(5) the dependence of the rate of filament growth on time is S-shaped;

(6) the time for the carbon filament formation depends on the reaction temperature: at 923 K, the growth of some filaments lasts for 10 min, while at 1243 K their growth stops after 30 s.

The catalytic particle at the end of the filament is pear-shaped.^{33, 35} An electron-transparent channel often passes along the entire filament length to its top. Reasonably, the filament has an external layer which is more resistant to oxidation than the internal one. The thickness of the external layer makes up $\sim 10\%$ of the outer diameter.

In order to understand the regularities of formation of carbon filaments, it is necessary to answer at least the following questions.

(1) Why carbon atoms are formed predominantly on one crystal face of a metal particle and crystallise into graphite structures on other faces?

(2) What are the driving forces for the migration of carbon atoms to the sites of graphite phase formation and what are the peculiarities of the mass-transfer of carbon atoms?

(3) What are the conditions for the appearance of the graphite phase crystallisation centres and specific features of these centres?

(4) How do the crystallographic and crystallochemical features of metal particles influence the properties of graphite structures formed on them?

(5) What possibilities exist for the targeted formation of graphitic phases of different morphological types?

There are two explanations of the reasons for the transfer of carbon atoms from the front part of catalytic particles where they are formed to the rear side where the filament grows. Some investigators presume that this transfer occurs owing to the diffusion of carbon atoms over the surface of the catalytic particle.⁸¹ However, the more popular is another viewpoint according to which the growth of filamentous carbon occurs as a result of diffusion of carbon atoms in the bulk of the metal particle.^{33–35, 39, 82–91}

The mechanism of filamentous carbon growth proposed by Baker *et al.*^{33, 35} is presented schematically in Fig. 3. After formation of small metal particles on a support (Fig. 3a), deposition of amorphous carbon takes place at the site of particle contact with the support (Fig. 3b). The formation of amorphous carbon is explained by the gas-phase polymerisation of acetylene. At the same time, acetylene is decomposed on a metal particle surface, and the carbon atoms are dissolved in the bulk of the metal. Decomposition of acetylene and solubilisation of carbon are accompanied by heat release, and this creates temperature gradient along the particle. Owing to this gradient, carbon moves

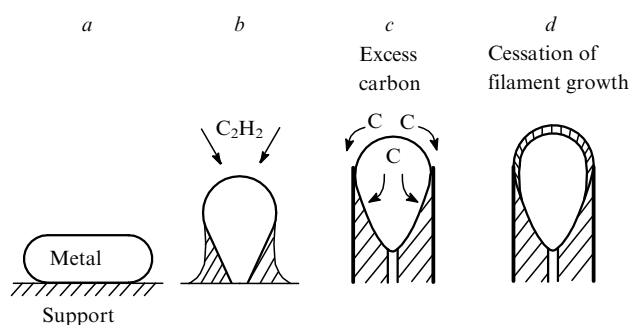


Figure 3. Schematic representation of the mechanism of the filamentous carbon growth from acetylene on a metal (see the text for comments).

to a colder part of the particle in contact with the support. The deposited carbon raises the metal particle and removes it from the support. The initial filament growth causes curvature of the metal particle which becomes pear-shaped, and this in turn leads to the formation of a channel (Fig. 3c). The increase in the filament growth rate is explained by the insulation of the particle from the support and the corresponding increase in the temperature gradient. The excess carbon formed on the outer surface of the particle migrates from this surface and builds the external wall of the filament. It is presumed that the external wall of the filament has a different structure from that of its core. The filament growth stops when the 'hot' side of the particle is covered by carbon (Fig. 3d).

In the authors' opinion,³⁵ their hypothesis is confirmed by the fact that the activation energies of the growth of carbon filaments on α -Fe, Co, Cr and Ni are close to the activation energies of carbon diffusion in the bulk of the corresponding metal. However, the values of the growth rates of carbon filaments on different metals^{33, 35} are contradictory. If the formation of filaments is governed only by the diffusion of carbon atoms in the corresponding metal, then under the same experimental conditions (1010 K, acetylene as the carbon source, catalytic particles of the same sizes), the growth rates should be proportional to the diffusion coefficient of carbon atoms in the corresponding metal. As noted above, the coefficient of carbon diffusion in metallic iron is 2–3 orders of magnitude larger than that in cobalt or nickel. Consequently, the rate of growth of carbon filaments on iron should be proportionally higher. However, in practice it proved to be lower on iron than on nickel or cobalt.^{33, 35} In this context, it is reasonable to suggest that the limiting step on iron is the interaction of acetylene with the surface of the metal.

The driving force of diffusion was presumed^{33, 35} to be the temperature gradient arising between the sites where the decomposition of hydrocarbons occurs and the sites where the graphite phase grows. The higher the metal temperature the larger the solubility of carbon in it; for this reason, concentration gradient also appears.

The concept according to which the growth of filamentous carbon is brought about by carbon diffusion in a crystal has been accepted by most investigators, whereas the appearance of mass gradient determined by the temperature gradient has become the subject of lively discussion.^{81, 82, 84–87, 92} The arguments of the opponents were based on the fact that the hydrocarbons, the decomposition of which is an endothermic process (*e.g.*, methane), also provide the growth of carbon filaments. The suggestion according to which the deposition of carbon is explained by the presence of admixtures of other hydrocarbons in methane was disproved by the fact that with high-purity methane (99.99 vol.%) the degree of its decomposition reached 30%.⁸⁷

In order to assess the magnitude of the temperature gradient, Tibbetts *et al.*⁹³ have simulated the process of the growth of the carbon filaments from acetylene on γ -Fe. To simplify calculations, they suggested that the filament has no hollow channel and its

diameter is equal to the diameter of the metal crystal initiating the filament growth. The thermal balance of the growing filament end was calculated on the assumption that all the heat released in the decomposition of hydrocarbons is absorbed by the metal particle. Calculations showed that the temperature gradient is smaller than 2×10^{-3} K, and such a small magnitude cannot ensure the really observed growth rates of carbon filaments. Nonetheless, unsuccessful attempts were undertaken to prove a substantial influence of the temperature gradient.^{94–96}

An alternative explanation of the nature of the driving force of diffusion is based on the appearance of concentration gradient. In the model proposed by Rostrup-Nielsen and Trimm,⁹⁷ it was suggested that the solubility of carbon at the hydrocarbon–metal boundary is higher than that at the metal–graphite boundary. However, the data on solubility used in this model and based on the results reported by Wada *et al.*⁸⁸ are questionable.

The hypothesis of concentration gradient was also supported by the authors of a series of studies,^{98–100} who investigated the growth of filamentous carbon upon disproportionation of CO on Co/Fe alloys. It was presumed that the activity of carbon at the gas–metal interface is determined by the carbon activity in the gas phase. The activity of carbon at the metal–filament interface was assumed to be equal to the activity of graphite. On the basis of this simple assumption, a kinetic equation was deduced according to which the rate of carbon deposition depends linearly on the carbon activity in the gas phase. However, the explanation of the reasons for the appearance of the concentration gradient^{97–100} appears to be supported with insufficient argumentation.

Based on the carbide cycle mechanism, a model of the filamentous carbon growth was constructed which does not contradict most experimental results.^{5,6,15} We believe that the mass-transfer of carbon atoms occurs owing to their diffusion in the bulk of metal particles from the formation site to the crystallisation centres. Depending on the ratios of the rates of formation and diffusion of carbon atoms, the limiting steps of the process may be different. Let us consider the growth of carbon filaments under the conditions where the limiting step is the diffusion of carbon atoms in the metal particle.

In a saturated solution, the solid and dissolved phases possessing equal chemical potentials are in equilibrium. In our case, however, carbon on the front and rear sides of the metal particle is in different states which are characterised by different chemical potentials. The pool of carbon on the front side of the particle is continually replenished due to the decomposition of hydrocarbons. On the rear side, carbon is formed as the graphite phase. The concentrations of saturation (solubility) of carbon at these sites are substantially different; therefore, a concentration gradient arises, which ensures continuous dissolution of carbon on the front side and its diffusive mass-transfer to the rear side of the metal particle. This gradient is rather high. The concentration of carbon atoms on the front side of the nickel particle formed by decomposition of intermediate carbide-like compounds is close to the concentration of carbon in Ni_3C carbide, *i.e.*, it reaches 25 at. %. This value is confirmed by the calculation of the linear rate of carbon filament growth.¹⁵

The linear rate of the carbon filament growth (V) is determined by the amount of carbon Q which has diffused through an area section unit of a metal particle in unit time.

$$Q = \frac{D(c_1 - c_2)}{L} \text{ and } V = \frac{D(c_1 - c_2)}{Ld},$$

where D is the coefficient of carbon diffusion in the metal, c_1 is the carbon concentration in the surface carbide-like compound, c_2 is the carbon concentration in the saturated solution of carbon in nickel on the rear side of the metal particle, L is the diameter of the metal particle at the end of the filament, d is the density of graphite.

These formulae were used to calculate the rates of the growth of carbon filaments 600 Å in diameter on metallic nickel at 873 K.

Decomposition of an intermediate carbide-like compound of the Ni_3C type gives the concentration $c_1 = 0.514 \text{ g cm}^{-3}$; the values of $c_2 = 3.8 \times 10^{-3} \text{ g cm}^{-3}$, $D = 3.89 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, $d = 2 \text{ g cm}^{-3}$ were taken from the monograph of Buyanov.⁵ The growth rate of carbon filaments found (1650 Å s^{-1}) is close to the values measured experimentally^{33,34} ($800–1600 \text{ Å s}^{-1}$).

An analogous explanation of the reasons for the diffusion of carbon atoms in the metal particle is given in Refs 101–107.

At present, the concept of the formation of carbon filaments by carbide cycle mechanisms is commonly accepted for the iron subgroup metals and their alloys.¹⁰⁸

3. The effect of the orientation of faces of metal single crystals on the growth of carbon filaments

Detailed crystallographic studies of the role of the orientation of catalytic particles in the preparation of filamentous carbon were carried out by Audier *et al.*^{98–100,109–115} using mainly the disproportionation reaction of CO on Fe–Co and Fe–Ni alloys. It turned out that on all alloys with the body-centred cubic (BCC) structure, the carbon filaments are formed; the metal particles which initiate their growth are oriented in such a manner that the direction [100] of single crystals is parallel to the filament axis. The (100) face of the crystal is free from carbon. The alloys with the face-centred cubic (FCC) structure also catalysed the growth of filaments; however, they had a different orientation relative to the carbon filament. The direction [110] of crystals was always parallel to the filament axis.

Electron microscopy studies of the metal particle–filamentous carbon interface showed^{98–100,109–116} that the liberation of carbon and generation of graphite layers occur on the vicinal faces of the catalyst particle. Near the metal–carbon interface, the graphite planes are arranged essentially parallel to the metal surface. The experiments were performed under the following conditions: the gas phase was compressed (75% CO and 25% CO_2), the pressure was 10^5 Pa and the temperature range was 723–923 K.

However, an investigation of the structure and texture of the filamentous carbon obtained from benzene on iron and from buta-1,3-diene on nickel showed⁷⁷ that the particles of metallic iron are oriented differently relative to the filament axis. The iron particles which initiated the growth of filaments were single crystals in which it was the direction [110] that was parallel to the filament axis. Analogous results were obtained later by Rodríguez *et al.*¹¹⁷ In crystals of metallic nickel the direction [100] was parallel to the filament axis, while the planes (100) and (110) were free from carbon. Similar orientation and disposition of faces were established by Yang and Chen.⁹⁴ Such an orientation of metal crystals and the presence of low-index faces in them are not occasional. Different faces possess different activities in the decomposition of hydrocarbons; the diffusion rate of carbon atoms through single crystals of metals can also be anisotropic.⁷⁷

Thus, different faces and sites of the surface of metal crystals where the mechanism of the carbide cycle of decomposition of hydrocarbons is valid are not equivalent and they exhibit different properties in the general process of formation of carbon deposits. The distinction between the adsorption and catalytic properties of different faces and surface sites is confirmed by numerous data. For example, in the studies of methane decomposition on nickel in the temperature range 300–773 K it was found^{56,118,119} that this reaction proceeded only on the faces (100) and (110) [but not on the (111) face]. At temperatures up to 673 K, surface carbide structures are formed on the surface of these faces and diffusion of the carbon formed in the bulk of nickel crystal becomes noticeable above 573 K. No chemisorption of methane or formation of carbon on the (111) face could be detected.

Decomposition of ethylene on the nickel faces (111), (110) and $5(111) \times (110)$ is yet another example.¹²⁰ On the stepped faces $5(111) \times (110)$, the cleavage of bonds occurs in the lower temperature range than on the smooth faces (111) and (110).

Presumably,^{77–79} the generation of the graphite phase is easier on the face (111) than on the faces (100) and (110) because of high degree of its geometric correspondence to the structure of the basal graphite plane. This conclusion is in good agreement with the results reported by Eizenberg and Blakely¹²¹ who studied the isolation of carbon from a supersaturated Ni–C solution on the faces (111), (311), (110), (210) and (110) and the vicinal high-index surfaces of nickel. In the course of the monolayer filling, the vicinal surfaces of nickel are spontaneously restructured (faceted) into stepped faces formed by the terraces (111) and the monoatomic steps (110) or (310) depending on the index of the initial face.

4. Steps of the growth of carbon filaments from methane on nickel-containing catalysts

Four individual sites (stages) which differ in the features of the carbon filament growth can be distinguished on the kinetic curves describing the decomposition of methane on the catalyst containing 85 mass % of Ni/Al₂O₃¹²² at 823 K. Analogous stages were observed in the formation of carbon from acetylene.²⁷

Crystals of nickel of various shapes are formed after the reduction of an aluminium–nickel catalyst. In conformity with the carbide cycle mechanism, the carbon atoms liberated as a result of methane decomposition in the induction period of filament growth diffuse into the bulk of the metal and form there a supersaturated solution of carbon in nickel relative to the graphite phase. As soon as the critical level of supersaturation is reached and a crystalline graphite nucleus appears at some site, condensation of the carbon atoms from the supersaturated solution occurs on the nucleus formed. In this case, the concentration of dissolved carbon in the zone adjoining the graphite phase decreases to its level in the saturated solution. The (111) faces of nickel are the most favourable for the formation of graphite nuclei, since the symmetry and parameters of the flat networks (111) of nickel (Fig. 4a) and (002) of graphite coincide. The graphite filaments formed upon carbonisation of Ni/MgO or Ni/Al₂O₃ catalysts have a coaxial conical structure where the graphite (002) layers are inserted one into another as funnels (see Fig. 2b). The correspondence of the structures of the face surface of nickel particles and the graphite filament can serve as a virtually classical example. It was shown⁶³ that the frontal side of a nickel crystal is formed by the (100) and (110) faces, while the faces (111) form its rear part.

After the appearance of the graphite crystallisation centres, the growth of graphite filaments begins, which is accompanied by the reconstruction of metal particles. During this period, the rate of carbon formation comes to stationary level. The shape of the metal crystals depends substantially on the rate of liberation of carbon atoms, their mass-transfer and specific features of the graphite structure.¹²² The more intense the process the more labile is the structure of the metal particle.

Boellaard *et al.*¹⁰⁵ noted that the formation of carbon filaments with the coaxial-conical structure should result in slippage of the carbon layers relative each other. Due to irregular supply of carbon atoms to the back, rear side of a cone-like metal particle, the carbon layers lose the form of ideal cones, and the body of filaments acquires an imperfect graphite structure with numerous

defects, in particular with a considerable number of edge dislocations.

However, in our opinion, as the new graphite layers grow, the nickel particle should be lifted a little, while the (111) face of nickel and the basal graphite face should slide relative each other. Each new graphite plane slides to the central part of the carbon filament. Owing to high mobility of nickel atoms at the Ni–C interface, the surface metal atoms dislocate towards the filament axis, and this explains considerable transformation of the metal particle during the accelerated growth of the carbon layer observed on kinetic curves. In this case, the nickel particle (Fig. 4b) changes its shape (Fig. 4c). According to the crystallographic laws, the angle α between the faces (111) should be approximately equal to 71°. However, at 823 K the transfer of nickel atoms out to the ‘tail’ of the crystal occurs rather strongly, which decreases the angle α to 50–60°. It may be suggested that the relief of the above-mentioned faces is determined by the atomic steps which change the slope of the plane. The nickel particles which initiate the growth of filamentous carbon from methane on Ni/Al₂O₃, are well formed (see Fig. 4c). The face (100) is oriented towards the filament growth, while the faces (111) in the ‘tail’ part of the nickel crystal form a pyramid with its top facing the side opposite to the filament growth direction.⁶³

It is clear that after the induction period the appearance of new crystallisation centres at some sites of the metal surface becomes virtually impossible. As a result, the site where the graphite growth occurs becomes the back (rear) side of the particle, while all the other faces, which are not closed by graphite, begin to play the role of the front side on which methane is decomposed by the carbide cycle mechanism. At relatively low temperatures of 748–798 K, such a form of nickel crystal remains invariable for a long time, which ensures stable growth of filamentous carbon. This stage is associated with the steady-state period of the filamentous carbon growth.

The velocity of filamentous carbon growth from methane at 823 K was estimated on the basis of the rate of carbon formation. Rather simple calculations¹²² showed that the mean filament growth velocity is 6 Å s^{–1}, while the carbon concentration on the front side of the nickel particle is only 2–3 times higher than that in the saturated solution in nickel at 823 K. It should be remembered that these results refer to the decomposition of the most stable hydrocarbon, *viz.*, methane. Therefore, in this case the limiting step is the decomposition of CH₄ molecules rather than the diffusive transfer of carbon atoms in the bulk of nickel particles. If the growth of filaments is limited by the diffusion of carbon in the bulk of the metal, then, as it was shown above, the gradient of carbon concentration becomes extremely large. This gradient predetermines the magnitude of diffusive flux of carbon atoms in the metal particle and has a strong effect on the phase state of the metal.

Transition metals (Fe, Co, Ni) have small atomic radii. In particular, it is 1.24 Å for nickel, and for this reason, the carbon atom with a radius of 0.77 Å is too large to occupy the octahedral voids of the most dense FCC-packing of nickel. Thus, diffusion of carbon through the nickel particle results in distortion of the crystal lattice of the latter. In some cases, the catalytic particle can become highly labile owing to a high carbon concentration, intense motion of carbon atoms through the metal bulk and the release of heat upon their condensation in the form of graphite phase.

Centres of carbon crystallisation on the metal particle are formed if a high energy barrier, which is 170 kJ mol^{–1} for nickel¹²³ and 220–300 kJ mol^{–1} for iron, is overcome.¹⁷ This is possible owing to a considerable supersaturation of carbon solutions in the metal which is especially large in the early stages of hydrocarbon decomposition. Studies using a high-temperature X-ray chamber showed¹²⁴ that in the course of induction period the concentration of carbon atoms on nickel exceeds 2 at.%.

Based on a thermodynamic analysis, Parmon¹²⁵ concluded that owing to a strong supersaturation of iron or nickel with

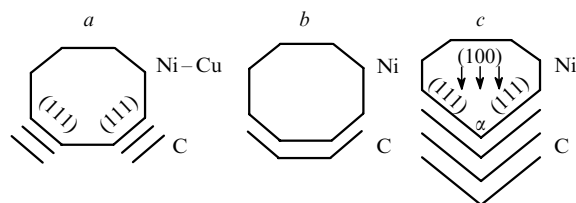


Figure 4. Schematic representation of a mechanism of the generation and growth of carbon filaments on Ni–Cu and Ni catalysts (see the text for comments).

carbon, which can reach > 10 mass %, melting of the metal should begin at ~ 920 K. In our opinion, this relates primarily to the induction period of the filamentous carbon growth because after the formation of graphite nuclei the maintenance of such a high carbon concentration in the metal is hardly probable.

The formation of carbon filaments is often associated with the high mobility of metal–carbon particles. In this connection, one should mention the VLS (vapour–liquid–solid) mechanism proposed for the description of the growth of silicon filaments on drops of a liquid metal.¹²⁶

The problem of the possibility of melting of metal particles has not been totally solved yet, and the temperature boundary where the metal particles catalysing the growth of filamentous carbon or nanotubes can pass to the liquid state, has not been established yet. Some authors state^{127, 128} that the finely dispersed catalytic particles of iron are capable of melting even at temperatures below 1173 K. They believe that the particles of liquid iron are ‘responsible’ for the efficient growth of carbon filaments. However, according to other data (see, *e.g.*, Refs 129 and 130), the ‘liquefaction’ of iron particles occurs at ~ 1400 K.

Relevant calculations confirm that the growth of carbon filaments from methane is initiated by edged particles oriented in a definite manner relative to the filament axis; the growth of carbon filaments from alkenes, dienes and acetylene is initiated by the pear-shaped particles, the form of which is less expressed.

In the so-called ‘extrusion’ method, which is less common than the above-considered (classical) method for the formation of carbon filaments, the crystal initiating the carbon deposition remains in contact with the support. This process occurs in the growth of carbon filaments on Pt/Fe alloys³⁶ and on pure metals.^{35, 131, 132}

5. Specific features of the formation of carbon filaments on metallic iron

In a number of cases, deposits of carbon on iron catalysts have the form of filaments.⁷⁷ A general view of such filaments is shown in Fig. 2*a*. Figure 5 shows a micrograph of one such filament. As a rule, the carbon filament contains inclusions both at end of the filament and in its hollow channel, which, according to micro-

diffraction data, represent the metal phase. Reflexes on electronograms indicate that this phase has a body-centred cubic lattice of α -Fe. The characteristic feature is that the crystallites which are constituents of the filament structure are oriented in a definite manner relative to its axis. The crystallographic direction of α -Fe [110] is parallel to the axis. The metallic inclusion at the end of the filament has usually the drop-like form, which is narrowed in its lower part and is weakly edged. The inclusions have a block structure. This follows from the existence of boundaries between the blocks as seen on electron micrographs and from the periodic contrasting of the areas of overlap of individual blocks.

The carbon of the filament is graphitised, and this is clearly seen in micrographs obtained by the high-resolution electron microscopy method. The distance between the planes is 3.5 ± 0.2 Å, which is close to the interplanar distance d_{002} for graphite. Zaikovskii *et al.*⁷⁷ showed that the graphite layers are concentrically arranged around the filament axis and the inter-channel metal particle.

The distribution of carbon around the metal particle at the end of the filament is irregular. The smallest thickness of the carbon layer (only a few monolayers) is observed on the side of the metal particle where the decomposition of a hydrocarbon occurs. As the distance from the top of the metal particle increases, the thickness of the carbon layer increases. The orientation of graphite layers at different sites of the metal surface is also different. In contrast to the upper part of the metal particle, in its lower part the graphite layers form a certain angle with the surface and are in contact with the metal by their terminal sides (Fig. 2*a*).

In the hollow channel of the filament there are very thin (2–10 monolayers) partitions composed of carbon layers.

Note in conclusion that the mechanism of generation and growth of carbon filaments on α -Fe is extremely complex. When considering these processes, one should take into account the following characteristic features of carbonisation of metallic iron:

- (1) high diffusion coefficient of carbon in the bulk of the metal ensuring its rapid supply to different surface sites;
- (2) incomplete epitaxial correspondence between the parameters of α -Fe face (111) and the basal graphite plane (002), which impedes the formation of nuclei of the graphite phase.
- (3) the tendency of metallic iron to form carbides.

6. Regularities of the formation of carbon deposits in the ‘octopus’ form

On nickel–copper alloys, the formation of unusual morphological ‘octopus’ carbon was observed.^{63, 106, 133–135} One particle of nickel–copper alloy initiates the growth of several filaments in different directions (Fig. 4*a*).

In contrast to nickel, metallic copper has low activity in the processes of carbon formation. It was used as an additive to Ni/MgO and Ni/Al₂O₃, because it has the same face-centred lattice like nickel and forms alloys with nickel in a wide range of concentrations. After reduction by hydrogen of the catalyst containing 10 mass % of MgO, 12 mass % of Cu and 78 mass % of Ni, the X-ray patterns reveal the predominance of the lines of MgO and a nickel–copper alloy of cubic structure⁶³ with the unit cell parameter $a = 3.53$ Å; this parameter corresponds to an alloy of approximate composition Ni_{0.9}Cu_{0.1}. The mean size of the alloy particles found from the half-width of the line (311) is 210 Å.

Kinetic studies of the formation of carbon from methane on the catalysts Ni/MgO and Ni–Cu/MgO showed that the rate of this process decreases as the content of copper in the sample increases.⁶³ Addition of 12 mass % of copper decreases this rate 2–3-fold. As a result, the aggregation of carbon atoms proceeds in a more ordered manner, and one observes a rather clear-cut trend towards the formation of graphite on the (111) face of the nickel–copper alloy (see Fig. 4*a*). The lattice parameter of the alloy increases with the increase in the copper content, and the crystallographic correspondence of the (111) faces of the alloy and the faces (002) of graphite becomes more and more complete.



Figure 5. A micrograph obtained by the method of high-resolution electron microscopy (HREM) of a carbon filament formed on metallic iron from an atmosphere of benzene diluted with argon in the molar ratio C₆H₆:Ar = 1:15 at 923 K.⁷⁷

Electron microscopy analysis showed^{63, 79, 133} that carbonisation of the Ni–Cu/MgO catalyst upon decomposition of methane for 1 min at 873 K leads to the formation of carbon filaments, the ends of which contain metal particles. This metal particle usually has a well edged form, while its diameter exceeds the diameter of the carbon filament. The data from electronic microdiffraction (EMD) suggest that the (111) face of the FCC lattice of the metal is the most developed. It is perpendicular to the direction of the filament growth and is in contact with the (002) planes of graphite. The lateral (100) faces of the alloy are free, they have no contact with carbon and are the centres of methane decomposition. The form presented in Fig. 4a corresponds to the initial stage of the growth of filamentous carbon on particles of the Ni–Cu alloy.

Carbon can be formed simultaneously on two opposite faces (111) of the flattened alloy particle; this can give birth to two carbon filaments in the form of rings containing a metal particle inside. Sometimes, carbon is deposited simultaneously on three (111) faces of a nickel–copper alloy and the growth of filaments begins in three directions (Fig. 6). According to the data from EMD, the structure of such filaments is formed by the graphite layer (002), arranged perpendicularly to the filament growth direction.^{63, 79, 133}

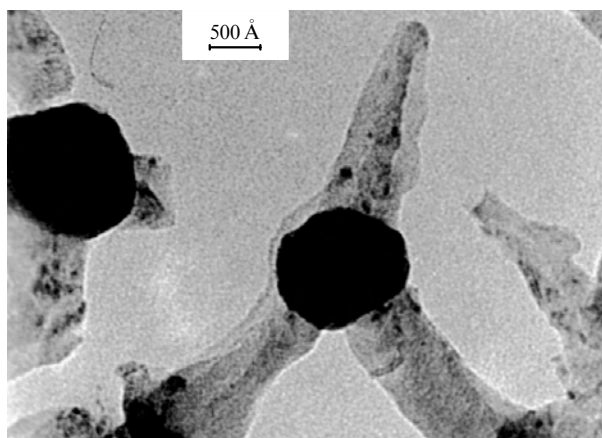


Figure 6. A micrograph showing the filamentous carbon growth in three directions on the Ni–Cu alloy particles.⁶³

The sizes and shapes of faces which determine the equilibrium habits are known to be related to the surface energies of these faces. The difference in the habits of catalytically active particles in nickel and nickel–copper catalysts is explained by different degrees of proximity of the parameters of hexagonal lattices of the nickel and nickel–copper alloys to the parameter of the graphite lattice. The link of carbon with a particle of nickel–copper alloy over the face (111) is stronger; consequently, the surface energy in this case is lower than on the nickel particle, and the size of (111) face is increased.

After carbonisation with methane for 2 min at 873 K the particles lose their clearly expressed edging.⁶³

The increase in the carbonisation time to 5 min induces changes in the structure of metal particles. It becomes of micro-block-type, the size of the blocks being 50–200 Å. The defectiveness of the alloy surface deteriorates the ordering of the graphite layers formed and in some places the filament is separated into layers (Fig. 7). This favours the formation of bundles of filaments growing from one particle. Very often, thin branches appear from the major bundle or from the block-polycrystalline metal particle. At the ends of such branchings, there are also metal particles.^{63, 79}

Carbon deposits, formed on the Ni–Cu/MgO catalyst upon decomposition of CH₄ for 3 h at 875 K present a porous mass consisting of filaments intertwined in a complex manner. In



Figure 7. Morphology of the carbon formed from methane on the block particle of Ni–Cu alloy after a 5-min relaxation at 873 K.

addition to large filamentous formations, numerous thin filaments 50–100 Å in diameter are present. Taking this into account, it may be concluded that large particles of the alloy break into individual blocks which catalyse the growth of thin filaments.

Thus, one of the stages in the formation of carbon deposits is the diffusion of carbon atoms in the metal particle determined by different concentrations of these atoms near those faces where a hydrocarbon is decomposed and graphite is condensed. The directed diffusion of carbon atoms at elevated temperatures leads to the displacement of the matrix atoms (Cu and Ni). This effect is the stronger the higher the ability of components to form chemical bonds with carbon. Stratification and fragmentation of a single crystal of the initial alloy in the process of the carbon filament growth may be explained by bulk diffusion of atoms. Consequently, as the carbon accumulates, the morphological structure of the carbon mass begins to resemble a branched tree.⁶³

7. The reasons for deactivation of a catalytic particle in the growth of a carbon filament

The phenomenon of deactivation of catalysts in their carbonisation by hydrocarbons has been investigated.^{5, 136} Deactivation is caused by destruction and grinding of catalysts, removal of some components from them and by the mechanical capture of individual microparticles by the growing carbon filaments. This phenomenon was called carbon erosion.

Electron microscopy studies of carbon filaments which ceased to grow showed that the front side of nickel particles is covered by a carbon film. Treatment of such filaments with hydrogen or oxygen leads to the recovery of their activity and continuation of growth.²⁷

In our view, the cessation of the filamentous carbon growth is explained by the peculiarities of the process itself. As noted above, the diffusion of carbon atoms in the nickel particle is determined by the existence of a concentration gradient. The concentration of carbon on the faces (100) and (110) on the frontal side of the crystal is larger than its equilibrium concentration at the nickel–graphite interface. Supersaturation of carbon solution in the metal is the driving force of structural transformations on the surface of nickel. The larger the supersaturation the faster the deactivation.

Wesner *et al.*¹³⁷ considered surface autodiffusion of carbon atoms on the (100) face of a nickel single crystal which is induced by catalytic hydrogenation of CO with the formation of methane. On this face, sinusoidal grooves 1 μm deep were made at a distance of 7 μm. After the catalytic hydrogenation of CO for 6 h, the shape of the section profile changed substantially. Faceting of the groove was spreading from the ridge down to the

'valleys'. Taking this into account, it may be suggested that the nickel atoms dislocate from the 'valleys' in the direction of ridge peaks with simultaneous creation of cutting. The height of ridges increases with time. There are grounds to believe that in the process of carbon deposition reconstruction occurs of the surface of the front side of the metal particle, on which the steps corresponding to the (111) faces appear. Thus, conditions are created for the formation of new graphite nuclei on the front side of the nickel crystal. Therefore, the front side of the nickel crystal becomes coated with a thin carbon film with time despite the efflux of carbon atoms inside the crystal. This is the primary mechanism of deactivation of metal particles which catalyse the growth of carbon filaments.

One manifestation of the carbon erosion is the destruction of metal particles initiating the growth of carbon filaments with the formation of smaller and smaller fragments which can eventually be totally 'overgrown' with carbon and become isolated. A spectacular example may be the above-described growth of filamentous carbon on the Ni–Cu alloy particles in the Ni–Cu/MgO catalyst. The initially formed filaments 500–1000 Å in diameter are branched with time. This is due to the fact that the diffusion flux of carbon atoms in the bulk of alloy particles favours their fragmentation and crushing into subcrystals, a part of nickel being removed with carbon. As the initial particle is fragmented, a deposition of carbon begins not only on major filaments, but also on the surfaces of a contact between individual subcrystals. As a consequence, the initial particles undergo the ever-increasing splitting, while each new smaller particle becomes the centre of the growth of new filaments of a smaller diameter. Gradual extinction of the process of carbon deposition is explained by the fact that the metal particles of some minimal size prove to be covered by a graphite envelope and are switched off the process.

8. The effect of carbonisation temperature on the regularities of growth of carbon filaments in the decomposition of methane on nickel and nickel–copper catalysts

The increase in the reaction temperature influences the peculiarities of the filamentous carbon growth on both nickel and nickel–copper catalysts. Figure 8 shows the kinetic curves of carbon formation from methane at different temperatures on an Ni–Cu/MgO catalyst (analogous kinetic curves were also obtained for an Ni/MgO catalyst).¹²² The rate of carbon formation increases with temperature. However, at 973 K the higher rate is maintained only for a few minutes, after which it drops abruptly. Figure 9 shows an electron micrograph of a filamentous carbon obtained from methane at 1023 K on an Ni/Al₂O₃ catalyst. It is seen that the nickel particles appear to stretch along the filament length. As a result, the channel inside the carbon filament is filled with metallic nickel. Analogous morphology is also characteristic of the filamentous carbon obtained from

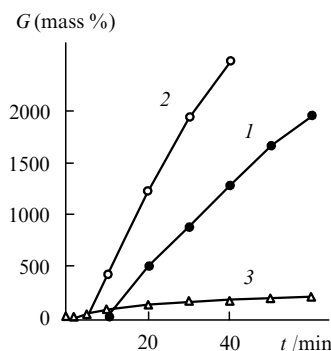


Figure 8. Kinetic curves of the carbon formation from methane on an Ni–Cu/MgO catalyst at 823 (1), 873 (2) and 973 K, respectively. *G* is the carbon increment.

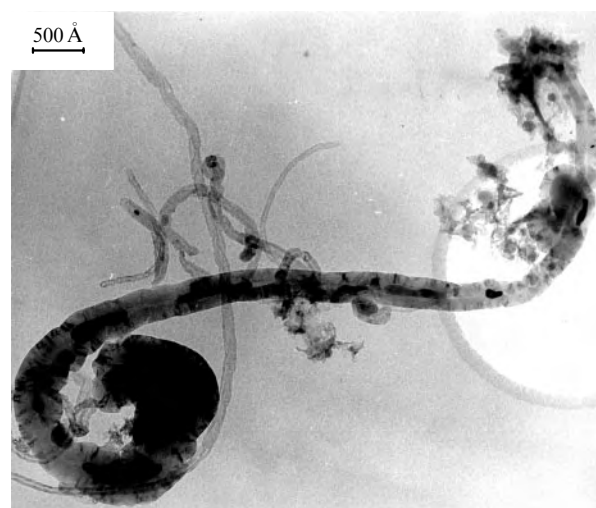


Figure 9. A micrograph of the filamentous carbon formed from methane on an Ni/Al₂O₃ catalyst at 1023 K.

methane on an Ni–Cu/MgO catalyst at 973 K. A question arises: what is the reason for the internal cavity formation in the graphite filament and what forces 'drag' the metal particle along this cavity?

The second mechanism of deactivation of metal particles which catalyse the growth of carbon filaments consists in the following. The increase in temperature and the higher rate of the filamentous carbon growth lead to an increase in the viscous fluidity of the metal particle, which facilitates sliding of the graphite planes formed over the surface of the metal¹²² and intensifies the efflux of nickel atoms in the direction of the diffusion flow of carbon atoms, *i.e.*, into the 'tail' part of the metal particle. As a result, the particle is elongated, while the angle α (Fig. 10 *a*) decreases considerably; the catalytic particle is transformed (Fig. 10 *b*). In the limit, the particle is so elongated that it acquires the shape of a needle (Fig. 11). Since in this case, the (111) faces become virtually parallel, the graphite deposited on them does not push the nickel crystal ahead but rather brings about lateral compression, which makes it still more elongated. Because of a large length of the nickel needle, the accumulation of carbon and supersaturation of the tail part in it proceed slowly. After reaching the critical supersaturation of the tail part of the nickel crystal, rapid condensation of carbon atoms begins with the formation of graphite layers which create carbon partitions inside the filaments. This in turn leads to irregular forward movement of the metal needle by pulsation. This results in the periodic appearance of carbon partitions which are seen in Fig. 11.

However, the situation changes considerably if carbonisation is carried out at 973 K in an atmosphere of methane diluted with hydrogen in the molar ratio 1:1. The morphology of the filamentous carbon formed on both Ni/Al₂O₃ and Ni–Cu/MgO

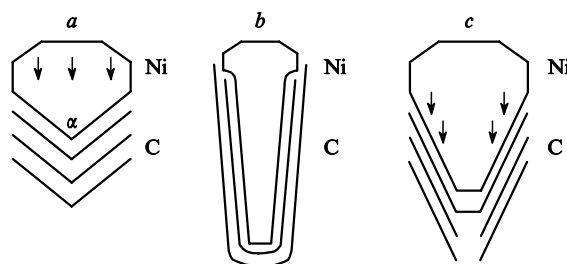


Figure 10. Transformation of catalytic particles upon the reaction temperature increase (see the text for comments).



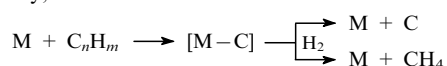
Figure 11. A micrograph of the filamentous carbon formed from methane on the Ni–Cu/MgO catalyst at 973 K.

becomes different. A hollow channel appears inside the carbon filament. (Fig. 10 *c*).

We have already mentioned that as the intensity of the process increases, the probability of restructuring of the metal becomes higher until some faces disappear and the other faces develop. In this case, upon addition of hydrogen to methane, the methanation of carbon atoms on the front side becomes possible. In other words, the reaction takes place which is opposite to methane decomposition, the carbon concentration on the front side decreases and the entire process is slowed down. It is logical to suggest that in this labile system reconstruction of the structure shown in Fig. 10 *a* into the structure shown in Fig. 10 *b* occurs. On the rear, a less active face (100) is formed in the side outgrowth; this is surrounded by more active sites (111).^{111, 113} The carbon is predominantly deposited at the sites marked with the arrows in Fig. 10 *c*, and this determines the speed of the motion of the entire particle. Thus, the reason for the appearance, along the filament axis, of a hollow channel the diameter of which is commensurable with the size of the 'passive' face (100) on the rear side of the particle is the stretching of the catalytic particle. Baker and Harris²⁷ explained the formation of a hollow channel by the slower supply of carbon atoms because of the increase in its diffusion route. However, this is rather the consequence of the catalytic particle stretching. The graphite layers which arise slowly on this face are sealed off periodically, making partitions in the hollow of the channel. At a more rapid influx of carbon atoms, the hollow channel should have filled with carbon.

9. The effect of hydrogen on the formation of carbon filaments

The knowledge of general regularities and specific features of the carbide cycle mechanism allows prediction of the influence of hydrogen on the deposition of carbon. Hydrogen can hydrogenate metal (M) carbides with the formation of lower hydrocarbons, mainly, methane:



Owing to this property, hydrogen also affects the formation of carbon; in the case of nickel, this effect is stronger than in the case of cobalt or iron.

Upon dilution of buta-1,3-diene with argon alone, the carbonisation of nickel proceeds rapidly at the beginning of the reaction, but then the rate of carbon deposition drops abruptly (Fig. 12). Addition of hydrogen decreases the initial rate of carbon formation. The larger the partial pressure of hydrogen in the reaction mixture the stronger is this decrease. At a partial hydrogen pressure p_{H_2} of 17.5 kPa, the rate becomes constant and does not depend on the carbon content on the catalyst. At higher pressures, an induction period appears the duration of which increases with

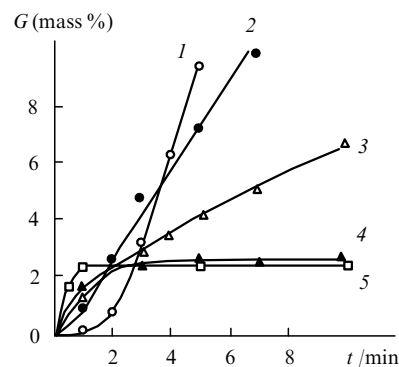


Figure 12. Effect of hydrogen on carbonisation of nickel by buta-1,3-diene at 698 K. The partial pressure of hydrogen/kPa: (1) 26.2; (2) 17.5; (3) 8.8; (4) 3.5; (5) 0.

p_{H_2} . If a hydrocarbon is diluted with hydrogen 300 times, the induction period will become so long that carbon will not be formed over 2 h.¹³⁸

An electron microscopy study showed¹²³ that carbon deposits formed upon dilution of a hydrocarbon with argon or hydrogen to $p_{H_2} = 17.5$ kPa, present mostly a film which screens the nickel surface. At a higher hydrogen pressure, carbon is deposited in the form of filaments which do not block the surface.

When carbonisation occurs in the medium of a pure or argon-diluted hydrocarbon, favourable conditions are provided for the appearance of the graphite nuclei, since in this case the carbon atoms do not have enough time to escape from the place of hydrocarbon decomposition. During subsequent growth of the nuclei, these atoms form a regular layer blocking the nickel surface.

Upon partial or complete replacement of an inert diluent by hydrogen, hydrogenation of an intermediate carbide-like compound begins to occur in addition to the hydrocarbon decomposition. At the same time, hydrogenation of carbon with atomic hydrogen formed as a result of the dissociation of H_2 molecules on the nickel surface becomes possible. As the partial pressure of hydrogen is increased, the hydrogenation rate increases. This decelerates the formation of the carbon phase nuclei on the surface accessible to hydrogen and leads to the appearance of an induction period. The activation energy of the graphite nuclei formation is 170 kJ mol^{-1} during the deposition of the first 1%–2% of carbon on nickel.

In a hydrocarbon–hydrogen medium, such nuclei are formed on the surface to which the access of reagents is hampered since hydrogen hydrogenates both the carbon atoms formed and the graphite nuclei. Owing to diffusion, a portion of carbon atoms is transferred to the interblock boundaries of nickel microcrystallites where new graphite nuclei are formed on defects.

Deposition of carbon on the interblock boundaries of nickel crystallites favours their dispersion and increases the number of metal particles which are actively involved in the interaction with the reaction medium. After the induction period and with the accumulation of graphite nuclei, the activation energy of carbon formation decreases and becomes constant (140 kJ mol^{-1}) after deposition of 10% of carbon. The transfer of carbon to the graphite phase nuclei (diffusion of carbon atoms in the metal bulk) becomes the limiting step of carbonisation. The value 140 kJ mol^{-1} is close to the reference value of the activation energy of the diffusion of carbon atoms in nickel.

Fragmentation of polycrystalline nickel into particles coated with carbon on the side inaccessible to the gas medium creates prerequisites for the formation of filamentous carbon. In this case, the carbon constituting the growing filament is not hydrogenated because hydrogen is virtually incapable of penetrating to the surface of contact of the metal particle with the carbon filament

phase (on the rear side), though a constant influx of carbon atoms takes place. The frontal (active) part of the metal particle, which catalyses the carbon filament growth, is not screened by carbon for the above-mentioned reasons.

Thus, the addition of hydrogen prevents the deposition of carbon in the form of a film and creates favourable conditions for the formation of carbon filaments.

Nolan *et al.*¹³⁹ gave an interesting explanation of the reasons for the formation of carbon deposits of different morphological types. They believe that carbon is accumulated as open forms, *e.g.*, carbon filaments, in the presence of hydrogen. The edge faces of graphite with unsaturated bonds come out, onto the external surface of the filaments, and hydrogen saturates these bonds. In the absence of hydrogen, carbon should be deposited predominantly in such forms as nanotubes or carbon films which do not have any unsaturated bonds on the edge faces. Thus the major products of decomposition of pure CO on highly dispersed nickel particles are carbon films and nanotubes, whereas the hydrogen-diluted CO forms carbon filaments with the coaxial-conical disposition of the graphite planes in the filament body. It is stated that the slope of the graphite cones depends on the hydrogen concentration in the reaction medium. However, in our opinion, Nolan *et al.*¹³⁹ give too much attention to the compensation of the energy of the free valences of the edge faces due to the formation of C–H bonds. It is unclear why CO₂ cannot react with carbon atoms and compensate thereby the energy of free valences. Furthermore, it is not taken into account that the neighbouring graphite layers coming onto the external surface of filaments can interact with each other thus closing the free valences.¹⁴⁰ Coming back to the role of hydrogen, let us note that it influences primarily the rate of the filamentous carbon growth, and this, as was shown above, changes the morphology of filaments.

10. The formation of carbon filaments at temperatures above 1273 K

The fibres used for the preparation of carbon composite materials are known to be obtained from viscose, polyacrylonitrile, as well as from petroleum or coal pitch. However, these materials have a substantial disadvantage — they are costly. Therefore, the prospect of their replacement by filaments prepared by catalytic methods seems rather attractive. A method for the preparation of carbon fibres from the gas phase [vapour-grown carbon fibres (VGCF)] is being actively developed in the USA, Japan and China.^{141–145} To this end, use is made of iron-containing catalysts deposited on ceramic supports or of injection of a benzene solution of ferrocene into a reactor. The sources of carbon are benzene or methane diluted with hydrogen as well as the gaseous waste from the production of coke or from the converter production of steel (CO–CO₂–H₂). A useful effect is given by the addition of small amounts of sulfur-containing gases (*e.g.*, H₂S) to the gas flow of reagents. The reaction is carried out at temperatures 1273–1423 K. The process starts with the catalytic growth of primary fibres, then they become thicker due to the deposition of pyrocarbon. The fibres prepared by the VGCF method have the following characteristics: length, a few millimetres; diameter, 2–3 µm; density, ~ 2 g cm⁻³.

Structural studies showed that the use of iron particles at temperatures above 1173 K can yield long filaments uniform in size, which consist of densely packed cylindrical basal graphite planes and always have a hollow core.

Baird *et al.*⁸¹ have proposed a scheme of the growth of a tubular filamentous carbon which presumes diffusion of small carbon clusters over the surface of a metal particle. This model was further developed in a study of Oberlin *et al.*,¹⁴⁶ which is one of the most detailed investigations of the structure of filamentous carbon formed from a benzene–hydrogen mixture at 1373 K. The reaction products were tubular filaments of cylindrical shape with a hollow channel inside them. The diameter of the channel ranged from 20 to 500 Å and was not always constant along the filament length. In their cross-sections, the filaments had a 'dendritic'

structure: apparently, the graphite layers formed concentric rings. In the core of the filament, the graphite structure was more ordered than in the outer layers. Based on the results obtained, the authors have postulated a two-step mechanism of the filamentous carbon formation. In the first step, the filament core is formed which consists of long parallel carbon layers twisted around the hollow central channel. In the second stage, the filamentous carbon becomes thicker owing to pyrolytic depositions. The ends of filaments contain the catalyst's particles. The interplanar distances measured by the method of electron microdiffraction make it possible to presume that the catalytic particles are either iron carbide (Fe₃C) or α-Fe. However, no final conclusions have been made.

Tibbetts¹⁴⁷ attempted to establish the reason for the tubular structure of carbon filaments. As the basal face possesses lower specific surface energy than the edge faces, the free energy of the growing filament should be a minimum when the filament consists of curved basal planes forming cylinders. However, as the diameters of cylinders decrease, the degree of curvature of the planes increases and, naturally, the energy required for such curving also increases. Thermodynamic considerations indicate that the formation of a hollow core is more advantageous energetically than the deposition of carbon in the form of strongly deformed cylindrical planes of small diameter. The model proposed made it possible to predict accurately the minimum inner diameter of a carbon filament and to substantiate theoretically the tubular structure of the filamentous carbon.

Deactivation of catalysts at high temperatures is associated with the blockage of the surface of catalytic particles; however, there are different suggestions about the mechanism of this phenomenon. Some investigators believe^{93, 147, 148} that deactivation is due to the adsorption, on the frontal side of the metal particle, of highly condensed pyrolysis products, which are formed in the gas phase and are precursors of soot particles. The equation obtained on the basis of this hypothesis provides a satisfactory description of the histogram of the distribution of filaments with respect to their length which are formed upon methane decomposition on γ-Fe at 1320 K. According to Gadelle,¹²⁸ the catalyst is active in the liquid state, and even small changes in the surface composition induce its transition to a less active non-melting form which is easily blocked by carbon.

11. Growth of carbon filaments under the action of catalytic particles present inside the filament

It was shown that disproportionation of CO on the Fe/Ni and Fe/Co alloys yields the so-called bifilaments.¹⁰⁰ It was established^{111, 112} that the growth of bifilaments is catalysed by biconical microcrystals. In their structures, each of the bicones is analogous to a 'simple cone' which initiates the growth of classical filaments. It was established that the directions [100] of the alloy crystal with the body-centred cubic lattice and [110] of the alloy with the face-centred cubic lattice are parallel to the filament axis. In the alloys with the face-centred cubic lattice, the twinning of biconical crystals was often observed. No simple mechanism has yet been proposed for the explanation of the growth of these unusual filaments.

12. Regularities and the mechanism of the growth of helical carbon forms

Helical filaments or bifilaments first described by Baker *et al.*³⁷ were formed on an Fe/Sn alloy from acetylene at temperatures above 1073 K. One catalytic particle of the alloy initiates simultaneous growth of two filaments in the opposite directions. The two corkscrew-like filaments grow with approximately the same velocities, and in the course of the process, identical fragments are reproduced symmetrically in either filament.

Unusual helical forms of filamentous carbon were also observed in the carbonisation of an Ni–Cu/MgO catalyst which was carried out in the medium of buta-1,3-diene diluted with argon and hydrogen in the molar ratio C₄H₆:Ar:H₂ = 2:40:75

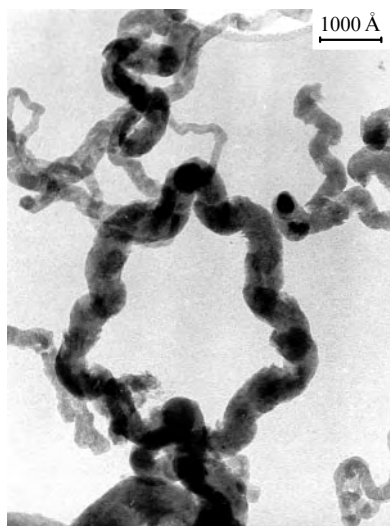


Figure 13. A micrograph of the mirror-symmetrical carbon filaments growing from one particle of an Ni–Cu alloy. Due to the increase in the carbon content on the Ni–Cu/MgO catalyst, its mass increased 28-fold (the same refers to Figs 14, 15).

at 723 K.¹⁴⁹ According to the X-ray diffraction data, after the reduction with hydrogen, the Ni–Cu alloy of cubic structure is predominant in the catalyst and the MgO phase is also present.

An electron micrograph of the mirror-symmetrical carbon filaments (Fig. 13) shows that the filaments are twisted into helices and originate from one metal particle. The thickness of these filaments ranges from 300 to 1000 Å, while their lengths reach 1 μm. Obtained by the HREM method, micrographs of metal particles on which carbon grows indicate (Fig. 14) that they possess a nearly symmetrical oval shape with the symmetry planes in the middle part and represent multiple twins. On the frontal side of the surface, in the middle of the oval metal particle there is a

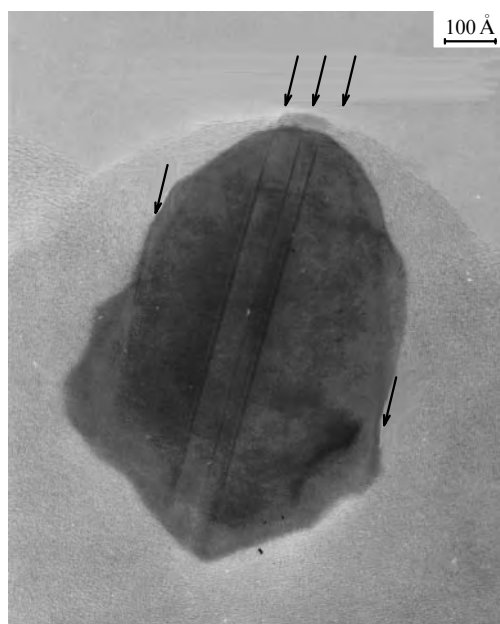


Figure 14. A micrograph obtained by the HREM method of an oval particle of an Ni–Cu alloy. The arrows indicate the positions of the twinning boundaries.

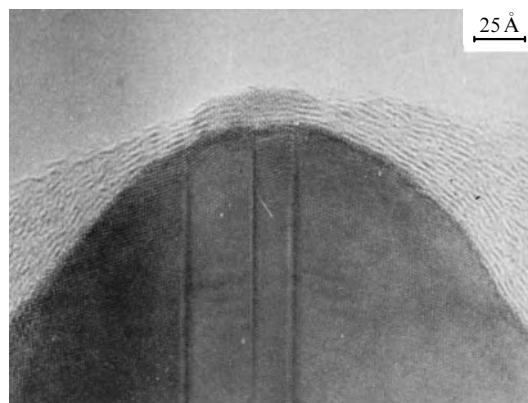


Figure 15. A micrograph obtained by the HREM method of the Ni–Cu/MgO catalyst.

microparticle 10–15 Å thick and 30–50 Å wide with the structure of the hexagonal nickel. It is on these microparticles that the ‘chemical’ step of the carbide cycle mechanism is realised.

In the crystalline particles of the Ni–Cu alloy, there is a series of twinning planes (111) which are parallel to the mirror symmetry plane. The twinning planes separate the blocks of twins with the face-centred cubic structure. The interplanar distances in each block of twins are: $d_{111} = 2.03$ Å and $d_{002} = 1.7$ Å. In a micrograph obtained by the HREM method, one can easily notice that the twinning planes are grouped under a microphase particle on the frontal side of the crystal (Fig. 15), while they are rarely found in other places. In the catalysts on which the deposition of carbon reaches 2000%–5000%, the widths of twin blocks in a metal usually exceed 20 Å.

At the beginning of the reaction the frequency of the appearance of twins in the metal is much higher than that at its end. In a micrograph of the Ni–Cu/MgO catalyst subjected to carbonisation for 10 min (Fig. 16), one can see the carbonisation boundaries with a period of ~4 Å. This distance is sufficient for the placement of only three densely packed layers of atoms of the face-centred cubic lattice of a metal with the interplanar distance $d_{111} = 2.03$ Å.

The hexagonal nickel carbide Ni_3C (see Ref. 150) and metallic nickel¹⁵¹ have virtually the same crystal lattices (hexagonal close packing). Carbon atoms in carbide occupy 1/3 of the octahedral cavities in the packing of metal atoms.

According to the mechanism of formation of symmetrical carbon filaments proposed by Zaikovskii *et al.*¹⁴⁹, in the induction

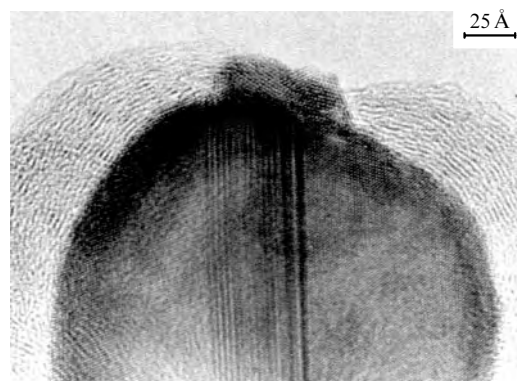


Figure 16. A micrograph of the Ni–Cu/MgO catalyst containing 75 mass. % of carbon. In the middle part of the Ni–Cu alloy particle one can see the boundaries of twinning after each 4 Å. The sequence of densely packed layers corresponds to the alternation of the hexagonal and cubic structures of the alloy.

period of the filamentous carbon growth, decomposition of buta-1,3-diene yields a particle of Ni_3C carbide microphase metastable at 723 K, while the Ni—Cu alloy itself is supersaturated with carbon. When critical supersaturation is attained and at some site of the alloy surface a crystalline graphite nucleus is formed, then a rapid ‘discharge’ of carbon atoms onto it occurs. The graphite phase nuclei are preferentially formed on the (111) face of the Ni—Cu alloy since the symmetry and interatomic distances in flat networks (002) of graphite and (111) of the alloy oriented towards the graphite filaments coincide.

Owing to a strong supersaturation of the frontal zone of the metal particle with carbon, an intense diffusion flux of carbon to the places of its crystallisation in the form of graphite phase arises. Rapid diffusion of carbon atoms leads to an enhanced generation of defects in the metal. The metal, while remaining solid, passes to the viscous-fluid state. As a result, the particle of the Ni—Cu alloy acquires spherical shape which is the most advantageous from the energetic viewpoint. However, the diffusive fluxes of carbon atoms also induce dislocation of metal atoms, and the spherical particle is somewhat stretched (Fig. 17). There arises a regime of self-organisation of the symmetrical form of metal particles. As a result, the metal particles acquire an oval form with the symmetry plane in their centre part. In this case, each of the symmetrical halves is oriented in such a manner that the [111] directions of the alloy coincide with the directions of the growth of carbon filaments.

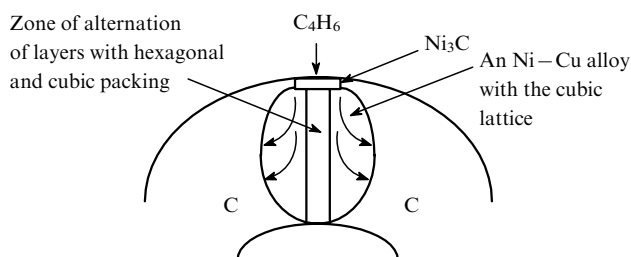


Figure 17. The mechanism of the growth of a helical carbon filament obtained from buta-1,3-diene on the Ni—Cu crystals.

A particle of the hexagonal Ni_3C carbide microphase on the frontal side is a nucleus for the growth of a hexagonal structure piercing the catalytic particle of the Ni—Cu alloy. Under the reaction conditions, the catalytic particle consists of alternating layers of cubic and hexagonal Ni—Cu alloys. The passage of carbon atoms through the interlayer of the hexagonal metal may be represented as continuously alternating steps of formation and decomposition of the carbide. However, the saturation of hexagonal interlayers with carbon should decrease as they go farther and farther from the microphase of the hexagonal carbide. Consequently, in the course of reaction the layers of the hexagonal metal include most probably a non-stoichiometric carbide of variable composition.

During the reaction, the twinning planes are dislocated from the central zone of the Ni—Cu alloy to the crystal periphery. The driving forces of the dislocation of the interblock boundaries and, respectively, of restructuring is the diffusion of carbon atoms and the lesser stability of the alloy with the hexagonal structure than that of the alloy with the cubic structure.

Owing to an intense directed flux of carbon atoms from the central part of the crystal to its periphery (see Fig. 17), defects arise in the layers adjoining the twinning planes which induce restructuring of the layers. In other words, the plane of twinning begins to dislocate in the direction of the movement of carbon atoms to the site of carbon crystallisation into the graphite phase. Thus, the hexagonal planar inclusions representing a non-stoichiometric carbide of variable composition ‘disperse’ from the middle of the oval metal—carbon particles. The removal of these

interlayers from the central zone is probably compensated by their repeated regeneration by a microparticle on the surface of a large oval particle in such a way that the process is continuous.

Graphite filaments grow symmetrically and virtually over the entire surface of the Ni—Cu alloy particle. The route of the diffusion of carbon atoms from the place of their entry into the alloy particle through the nickel carbide microphase to different sites of the graphite phase growth is not the same (see Fig. 17). Because of this, the velocities of the graphite phase growth become also different and twisting of filaments occurs to the side opposite to the place where the carbide microparticle is situated.

IV. Conclusion

The above-discussed observations and conclusions are helpful in understanding the factors that influence the process of carbon filament formation and determine their properties. These properties include primarily the spatial order of the construction of the basal graphite planes in filaments, the diameters and lengths of filaments, the presence or absence of the inner hollow along the axis of filaments, their morphologies, the existence and degree of dispersion of other mineral components in the graphite structure of filaments, etc. Adsorption, catalytic, chemical, magnetic, mechanical and many other properties of filaments depend on these characteristics.

Note that the methods for controlling the synthesis of carbon materials are still in their infancy. For this reason, we will touch upon this issue only in brief and in most general terms.

The most substantial effect on the properties of filamentous carbon materials is the spatial distribution of the basal planes of graphite. The distribution of graphite layers in a filament determines such properties of the carbon material as its mechanical strength, adsorption capacity, chemisorption and catalytic characteristics, intercalation capacity and others.

As mentioned above, depending on the properties of the catalytic metal particle (head) and conditions of the implementation of the process, it is possible to synthesise graphite filaments of three major ‘basal’ structural types: with the coaxial-cylindrical, coaxial-conical and stack structures (see Fig. 2). The properties of metal particles which are of interest to us can be regulated by varying the method of their preparation and by adding other metals.

The diameter of a filament is determined by the size of the metal particle and differs little from it. The length of a filament depends on the time of its growth, which in turn is determined by the time during which the metal particle can efficiently play the role of the filament growth centre without undergoing deactivation or breaking into subcrystals.

The regime of the process has a substantial effect on properties of carbon materials not only directly, but also indirectly, through deactivation of metal catalyst particles. A decrease in the temperature of the process, dilution of a hydrocarbon with hydrogen, use of a less coke-producing hydrocarbon will make it possible to increase the yield of carbon formations per unit mass of a metal and to improve the graphite structure. However, in this case, naturally, the rate of carbon formation decreases.

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^b — *Russ. J. Phys. Chem. (Engl. Transl.)*

^c — *Russ. J. Appl. Chem. (Engl. Transl.)*

^d — *Chem. Sustainable Dev. (Engl. Transl.)*

Synthesis and properties of functionalised dendrimers

I P Beletskaya, A V Chuchurjukin

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Abstract. The published data on the synthesis, structure, properties and applications of dendrimers containing conjugated π -systems, transition metal complexes and organometallic compounds are surveyed and systematised. The bibliography includes 83 references.

I. Introduction

The chemistry of dendritic molecules, which is a fundamentally new branch of chemistry, began to develop explosively in the past few years. The beauty of these flower- or star-shaped structures is so amazing that it may spark the imagination of artists. However, apart from the great attractiveness of these experimental subjects the interest of investigators in this field of chemistry is mainly due to the potential applications of dendrimers, for example, in industry as novel catalysts and materials for molecular electronic devices and light energy conversion, in medicine and in other fields.

In contrast with polymers formed by spontaneous polymerisation, dendrimers, which are oligomeric compounds (in principle, they can be polymeric), are prepared by multistep synthesis. There are two different methodologies, *viz.*, the divergent and convergent approaches. In the divergent approach, dendrimers are constructed by the attachment of various fragments to a dendritic backbone (core). In this case, the molecule is built up layer-by-layer in the direction from the centre of the dendritic molecule to its periphery. The convergent methodology involves initial synthesis of dendrons, *i.e.*, the branches of a dendrimer, which are then coupled to the dendrimer core. This process resembles the assembly of individual sections on a common base.

More complex dendritic molecules built out of individual fragments are constructed using methods of organic, organometallic or coordination chemistry employed for the preparation of supramolecular structures.

Dendrimers have been described in numerous reviews;^{1–12} however, the number of new types of dendritic molecules continues to increase. In writing this review, we were guided by our own interests and thus confined ourselves to the consideration of those dendrimers which incorporate ethynyl and aromatic fragments synthesised in reactions catalysed by transition metal complexes and dendrimers containing transition metal complexes as their cores or at the periphery where the metal is linked to the ligand by a coordination bond or by a carbon–metal bond. In many cases, we followed the path of the authors of the original publications who have discussed zero-generation molecules as matrices for future dendritic systems of the first, second and higher generations. It should be noted that our subdivision into sections is arbitrary, since many dendrimers comprise both arylethynyl fragments (which is the object of our particular interest) and transition metal atoms, leaving silicon-containing and many other dendrimers beyond the scope of consideration. In our attempt at a maximally complete coverage of the available material, we kept on adding novel data, but soon realised that we had to stop, otherwise this review would have never been written, for the number of publications is increasing every day.

II. Hydrocarbon dendrimers containing conjugated π -systems

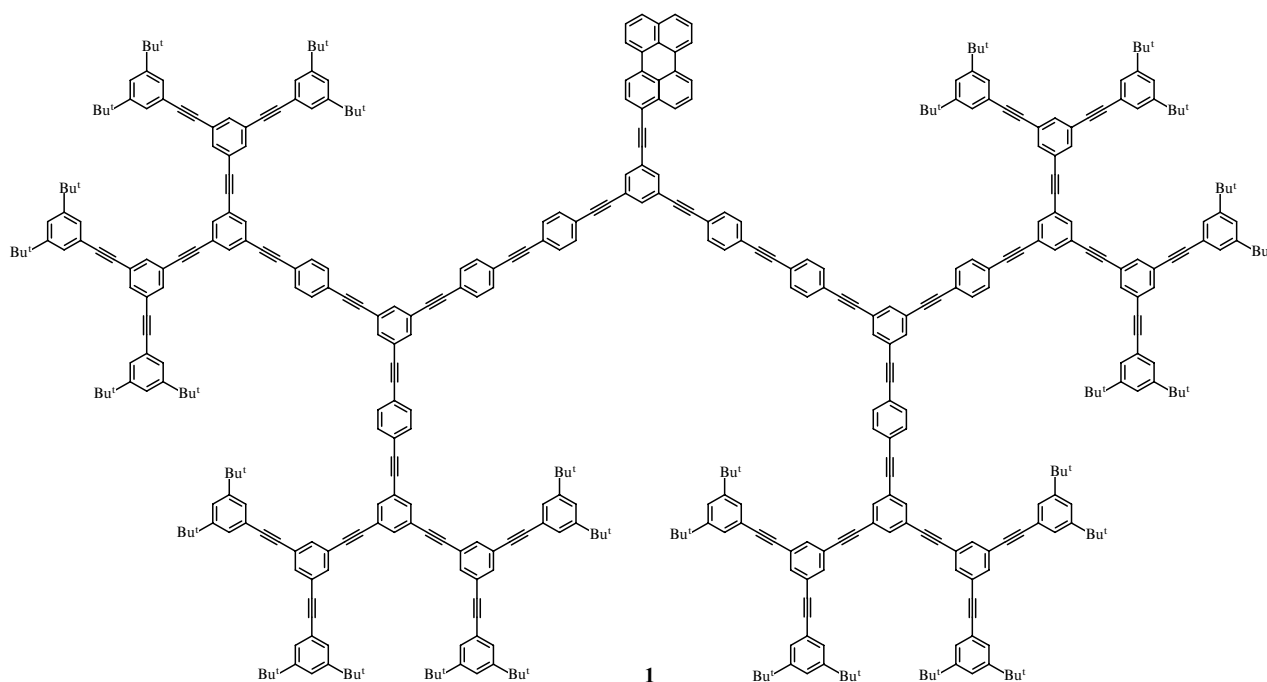
Cross-coupling reactions catalysed by palladium complexes are widely employed in the synthesis of dendrimers containing ethynyl or *p*-phenylene fragments. This type of dendrimer presents substantial practical interest because it ensures structural rigidity and conjugation between the fragments, which are essential for directed energy and electron transfer and for the preparation of photoreactive materials.^{13, 14} 1,3,5-Triethynylbenzene, which does not ensure conjugation between the substituents¹⁵ on the periphery, can nevertheless transfer photoexcitation energy^{13, 14} and represents a convenient core for the construction of such dendrimers. The photoreactive dendrimer **1**, the dendritic branches in which are linked together through ethynyl and *p*-phenylene bridges with a common focal point $\dagger$ of the dendrimer,¹⁶ *viz.*, the

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$\dagger$ By the term ‘focal point’, the terminal point of the photoexcitation energy transfer in the molecule is understood in this case.

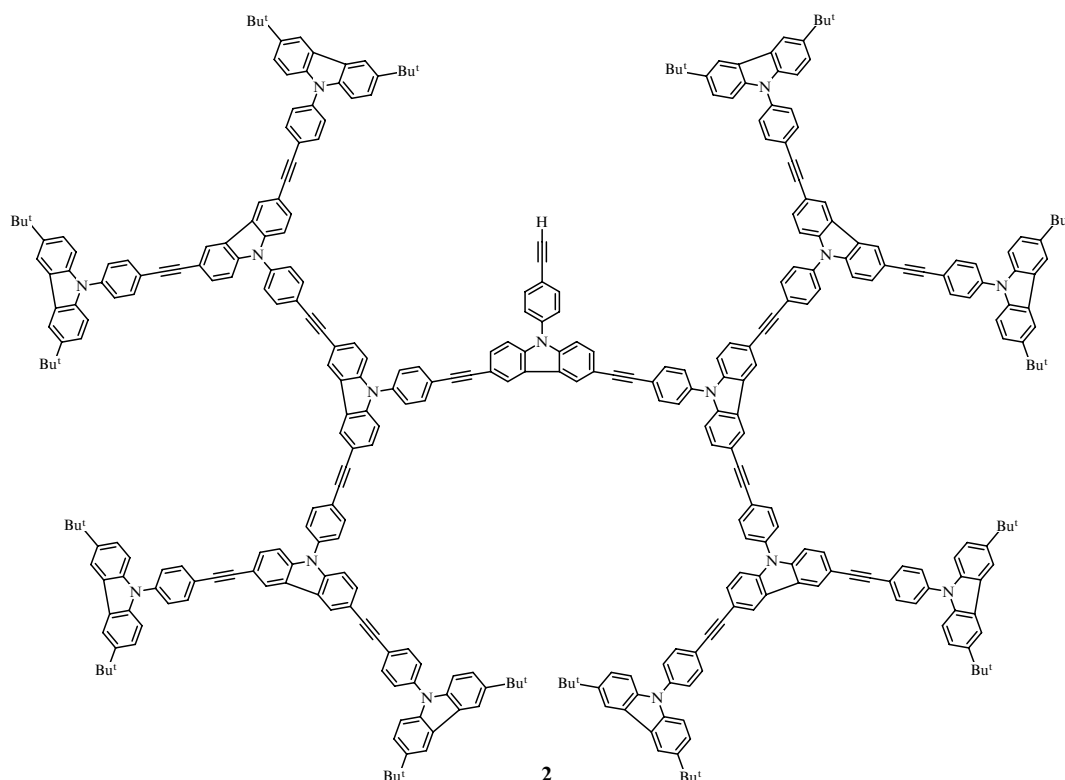


perylene fragment, may serve as an example. This dendrimer was synthesised by cross-coupling of a terminal acetylene with tribromobenzene according to the Sonogashira reaction.¹⁷ Studies of the photophysical properties of this dendrimer revealed that on irradiation with light with the wavelengths corresponding to the absorption maxima of peripheral triethynylbenzene groups, the radiation intensity of the perylene fragment in the dendrimer exceeds that of free ethynylperylene by more than two orders of magnitude under identical conditions. In this case, the efficiency

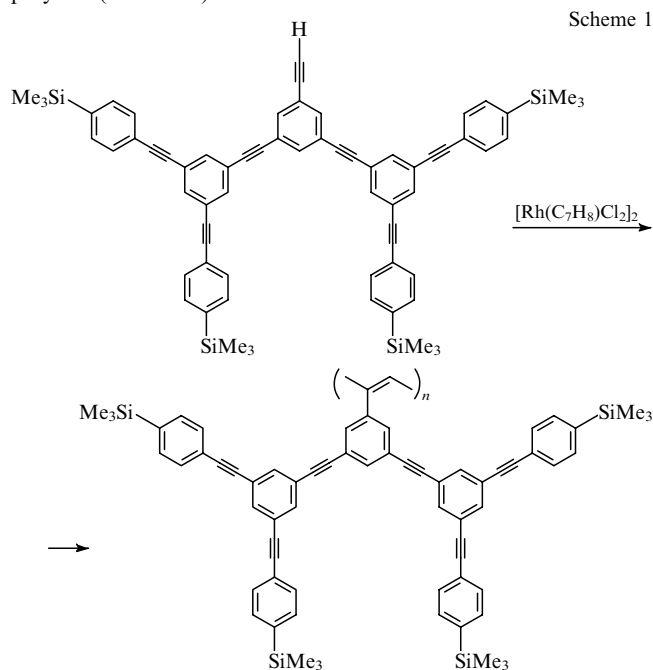
of the energy transfer from the periphery to the focal point of the dendrimer reaches 98%.¹⁶

Further investigations showed that the dendrimer of the next generation absorbs more light, but the efficiency of energy transfer to the focal point decreases.¹⁸

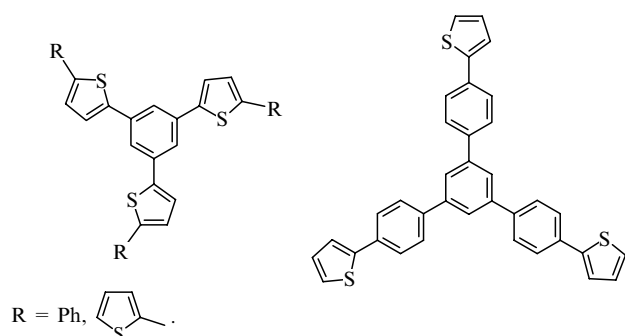
The dendrimers **2** containing 9-phenylcarbazole fragments linked through ethynyl bridges have been synthesised.¹⁹ Such dendrimers are designed for the preparation of organic photoconductors (*i.e.*, compounds with non-linear optical properties), photo- and electroluminescent materials.



A dendrimer containing 1,3,5-triethynylbenzene fragments was used as the monomer unit in the synthesis of a polyacetylenic polymer (Scheme 1).²⁰



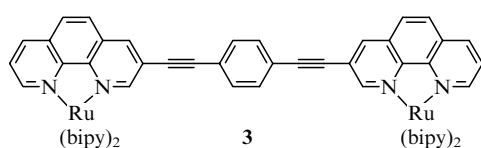
A series of zero-generation dendrimers containing thiophene groups were prepared by trimerisation of acetylthiophene derivatives in the presence of SiCl_4 .²¹



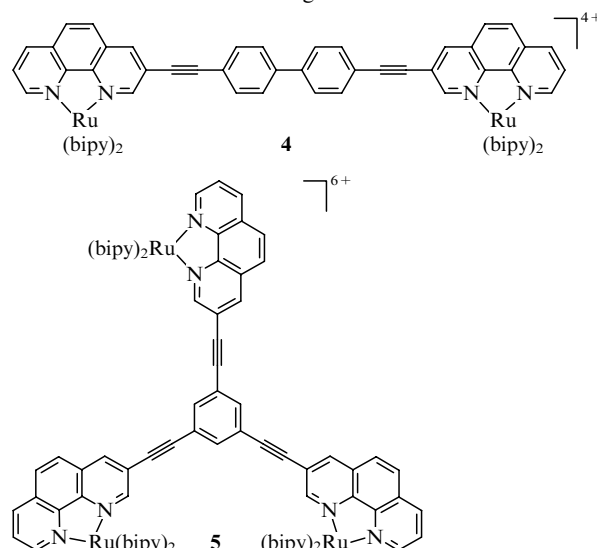
These compounds can be used in the synthesis of dendrimers, organic polymers of higher generations, semiconductors and liquid-crystalline materials.

III. Conjugated dendrimers containing transition metal atoms

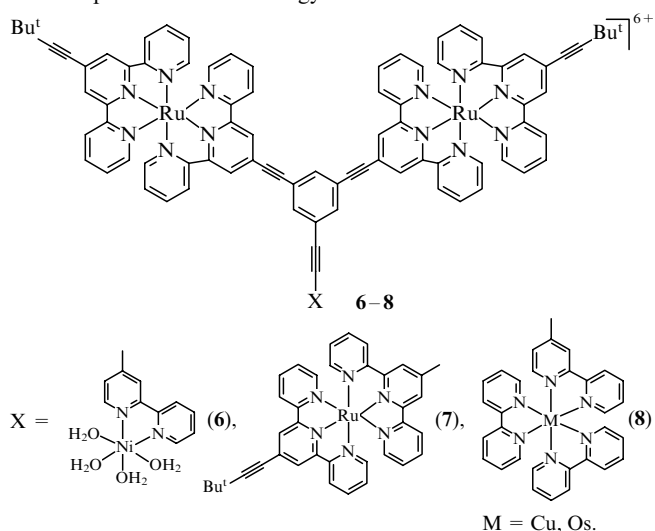
Conjugated systems, which contain several polydentate ligands coordinated to metal atoms within a single molecule, present substantial interest. Examples are provided by bi- (**3**, **4**) and trinuclear (**5**) complexes of ruthenium with a phenanthroline ligand synthesised by cross-coupling of a Ru–3-bromo-1,10-phenanthroline complex with 1,4-diethynylbenzene, 4,4'-diethynyl-1,1'-biphenyl and 1,3,5-triethynylbenzene, respectively.¹⁵



Measurements of the UV-spectra of the complexes thus prepared revealed that the main absorption bands of the bipyridine ligands do not change. Conjugation of the phenanthroline ligands in the binuclear complexes based on 1,4-diethynylbenzene (complex **3**) and 4,4'-diethynylbiphenyl (complex **4**) produced an additional low-energy absorption band. The absorption spectrum of the trinuclear complex **5** based on 1,3,5-triethynylbenzene more closely resembles that of the mononuclear complex, which points to the lack of conjugation between the substituents at positions 1, 3 and 5 of the central benzene ring.

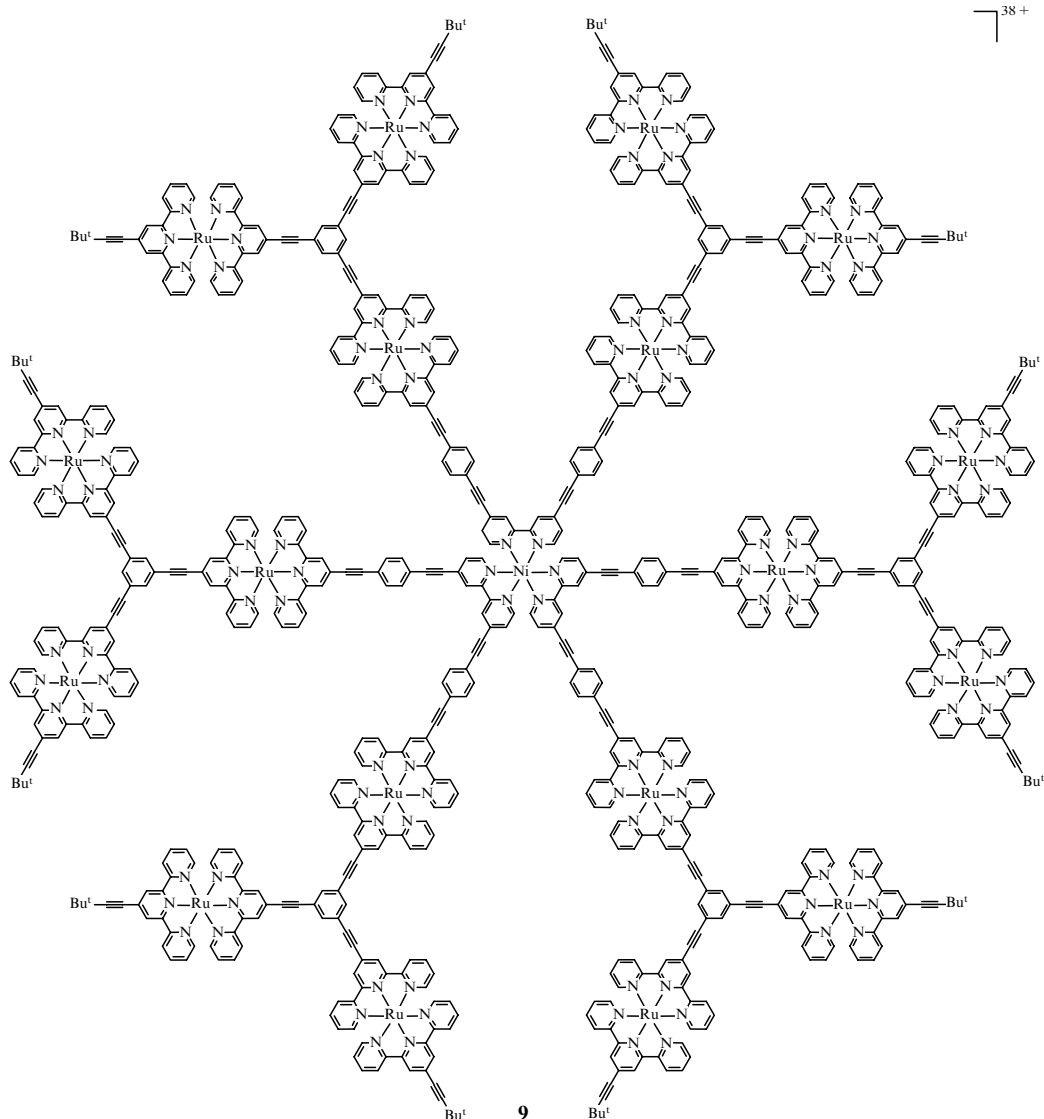


Luminescence studies of the heteronuclear complexes **6–8** containing both Ru and Ni, Ru and Cu or Ru and Os cations, which have been prepared by cross-coupling of Ru–phenanthroline complexes and the bipyridine complexes of Ni, Cu and Os with 1,3,5-triethynylbenzene, established that such complexes can transfer photoexcitation energy.¹³



Thus the fragment **7** was used to build a more complex molecule **9**¹⁴ in which the Ni–bipyridine complex is the central part of the molecular architecture. It is of note that the syntheses of complex molecules on the basis of fragments **6–8** have been accomplished with 67% to 78% yields.

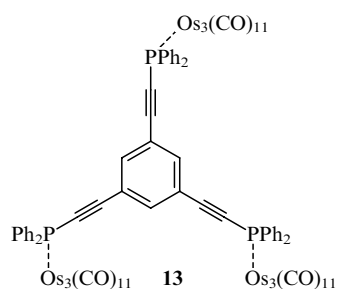
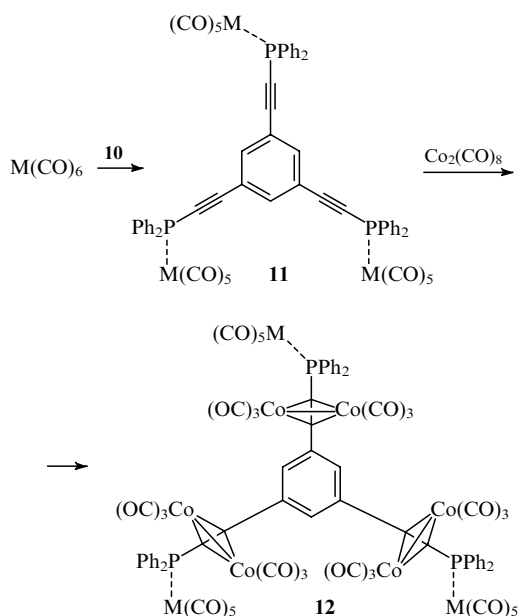
1,3,5-Triethynylbenzene was used as a basis for the synthesis of the tridentate phosphine ligand 1,3,5-($\text{Ph}_2\text{PC}\equiv\text{C}$) $_3\text{C}_6\text{H}_3$ (**10**). To this end, 1,3,5-triethynylbenzene was metallated with 3 equiv. of *n*-butyllithium and the lithium derivative formed was introduced into the reaction with chlorodiphenylphosphine.²² The



phosphine ligand **10** was first introduced into the reaction with the molybdenum or tungsten carbonyls $M(CO)_6$ ($M = Mo, W$) and

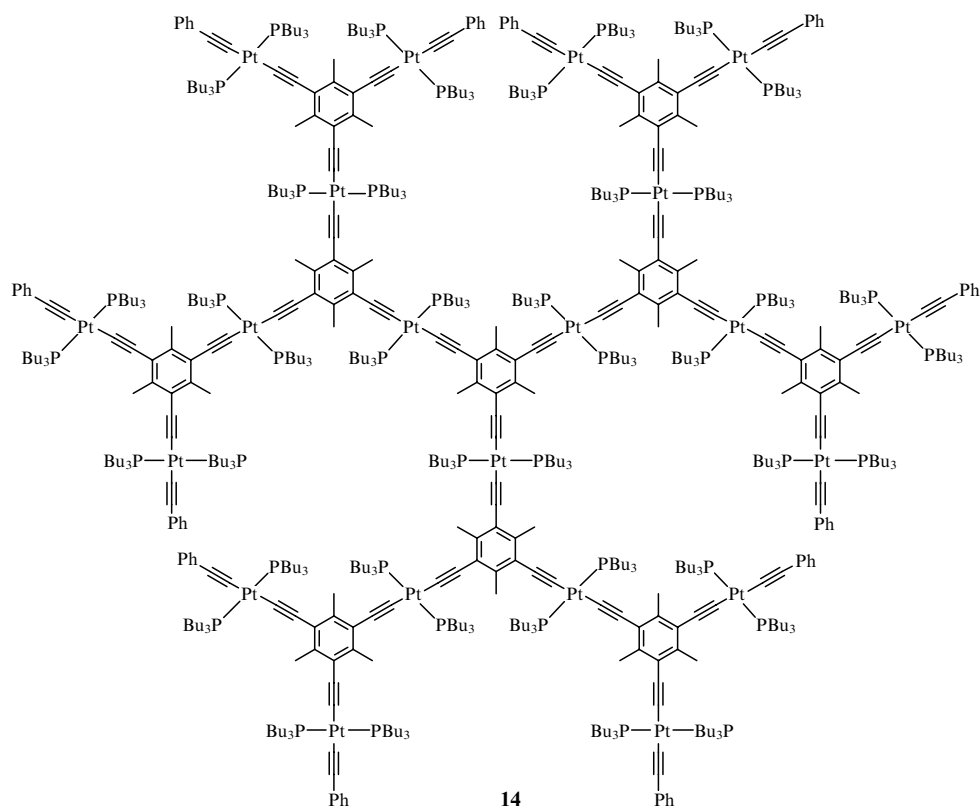
the complexes **11** formed were treated with cobalt carbonyl $Co_2(CO)_8$. These reactions afforded compound **12**.

The osmium complex **13** was obtained in a similar way. In the latter case, the phosphine ligand **10** was coordinated to three $Os_3(CO)_{11}$ clusters.



True organometallic compounds constitute an additional type of dendritic conjugated systems. The platinum complex **14** with triethynylmesitylene ligands prepared by cross-coupling of triiodomesitylene with trimethylsilylacetylene with subsequent desilylation is an example.²³

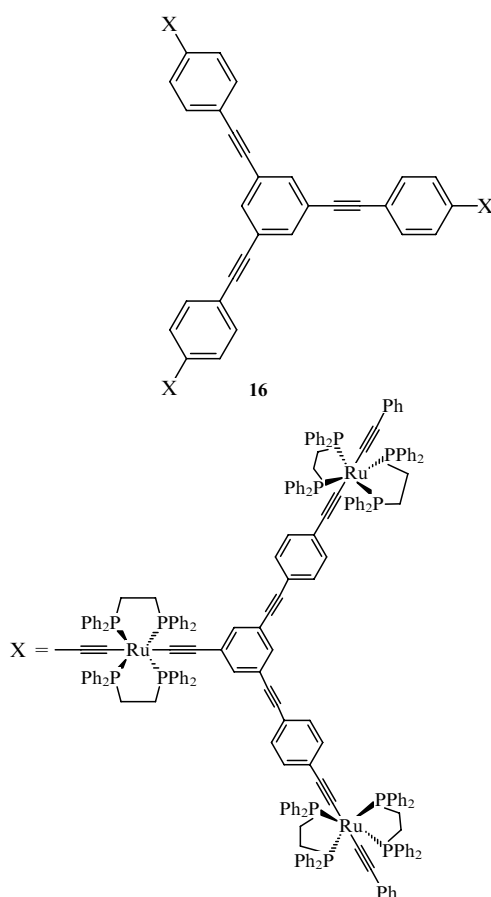
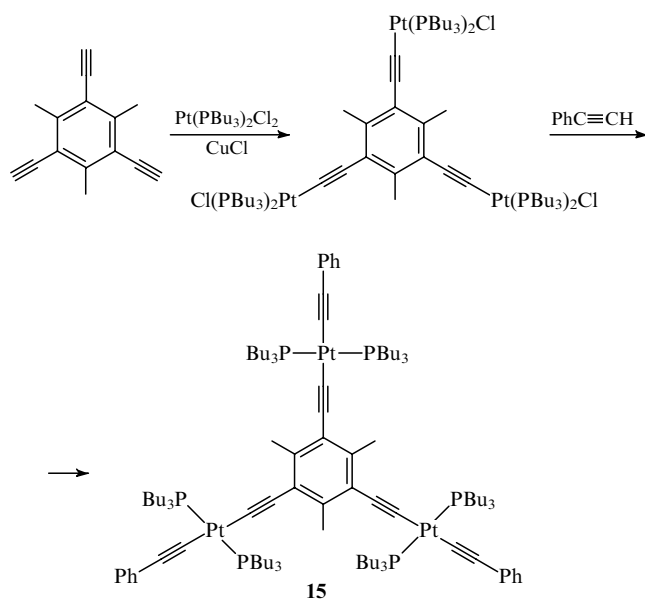
Triethynylmesitylene was introduced into the reaction with $Pt(Bu_3P)_2Cl_2$ in the presence of $CuCl$ and further converted into the complex **15** by a reaction with phenylacetylene. Substitution of



triethynylmesitylene for phenylacetylene yields first- and second-generation dendrimers.²³

The organoruthenium dendrimer **16** was synthesised following the convergent approach.²⁴ It was shown that the introduction of ruthenium atoms into a conjugated π -system significantly enhances both the non-linear optical properties of the original

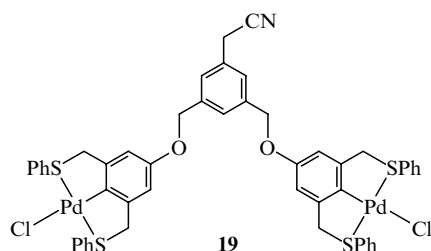
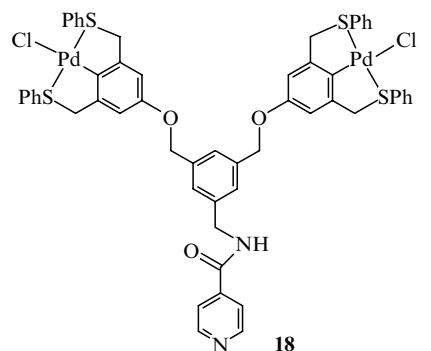
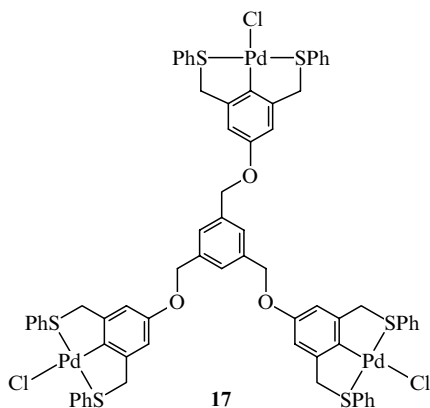
compound and the two-photon absorption. These characteristics are also enhanced with the growth of the dendrimer.



IV. Dendrimers containing pincer-type ligands and their metal complexes

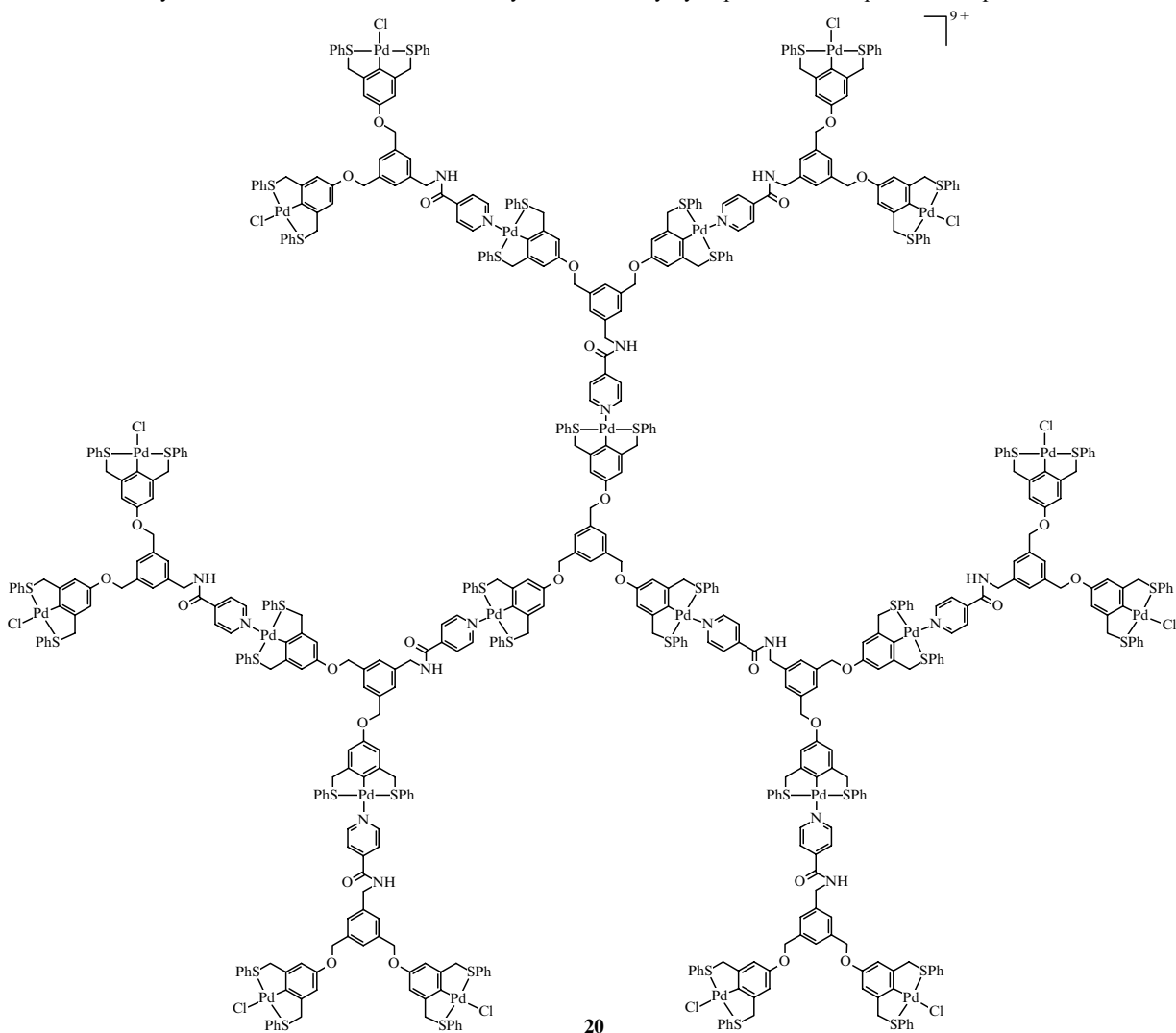
The presence of pincer-type ligands at the periphery of zero-generation dendrimers facilitates their metallation with the formation of metallacycles. Thus the complexes **17–19** containing pincer-type SCS ligands were used as building blocks in the synthesis of more complex dendrimers.^{25,26} For example, the pyridine group in compound **18** or the cyano group in compound

this case the pincer group is incorporated into the dendrimer structure as the connecting link.



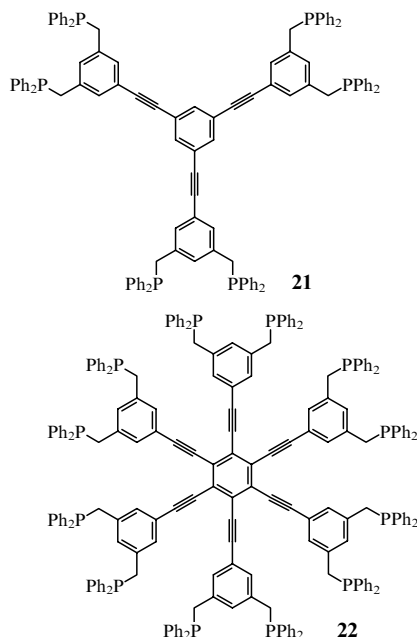
19 is coordinated to palladium atoms to yield cationic complexes. The dendrimer **20** synthesised on the basis of the complexes **17** and **18** represents an organometallic compound the dendritic structure of which is formed by coordination bonds. It is noteworthy that in

The presence of SCS pincer-type ligands strongly restricts the application of non-palladium transition metal complexes, since only cyclopalladation is possible. Replacement of SCS by PCP

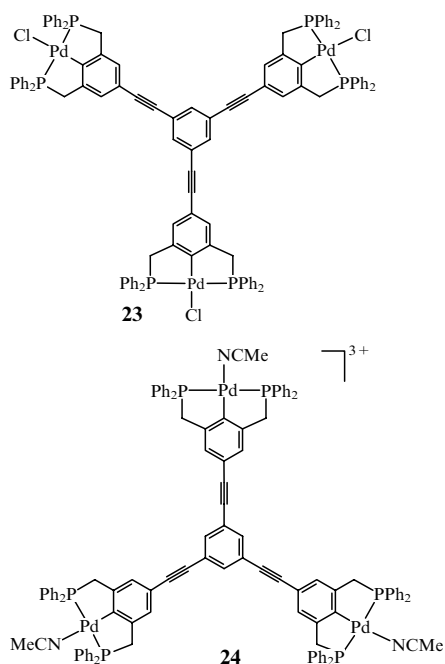


ligands made it possible to conduct cyclometallation with both Pd complexes and a variety of other transition metal compounds.

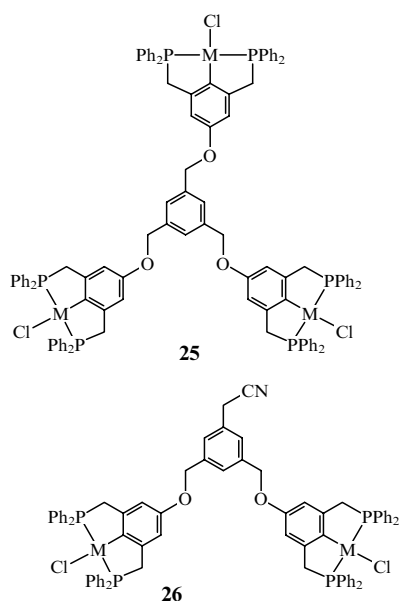
We made an attempt to synthesise zero-generation dendrimers on the basis of triethynylbenzene (**21**) and hexaethynylbenzene (**22**).^{27, 28}



Cyclopalladation of triethynylbenzene **21** was successful. The corresponding trinuclear palladium complex **23** was obtained in 90% yield. However, cyclopalladation of the ligand **22** designed for the synthesis of a hexanuclear complex failed, since this reaction gave a mixture of compounds. We attribute this failure to the high degree of conjugation within the molecule, which prevents the introduction of six electron-withdrawing substituents. Yet another trinuclear palladium complex **24** prepared by cyclopalladation of the ligand **21** is an efficient catalyst for the Heck reaction.²⁹

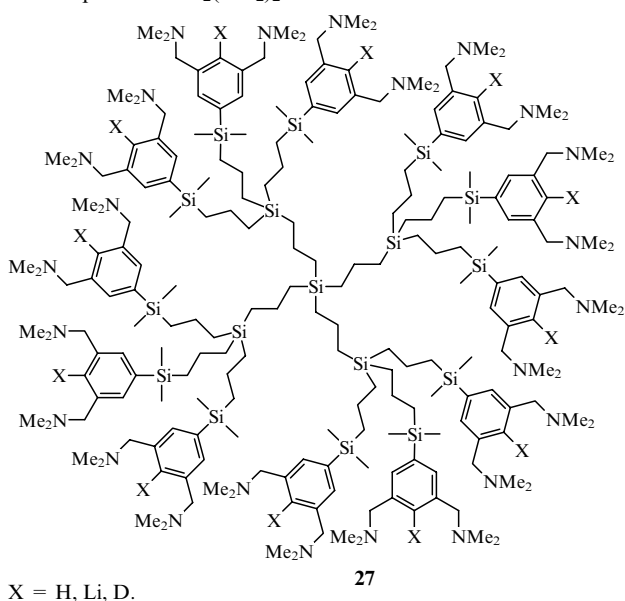


The applications of other transition metal complexes, *e.g.*, the Ni and Pt complexes **25** and **26** containing PCP pincer-type ligands, have been described.³⁰



M = Ni, Pt.

A method for the introduction of the pincer-type NCN and CN ligands, *e.g.*, 1-[3,5-(Me₂NCH₂)₂C₆H₃] and 1-(4-Me₂N-CH₂C₆H₄) units, at the periphery of organosilicon dendrimers of zero (G₀) and first (G₁) generations has been proposed.³¹ To this end, the corresponding bromo-substituted derivatives, *viz.*, 1-Br-3,5-(CH₂NMe₂)₂C₆H₃ or 1-Br-4-Me₂NCH₂C₆H₄, were lithiated and introduced into the reaction with an organosilicon dendrimer containing the chlorosilane groups Si(CH₂CH₂CH₂Cl)₃ at the periphery. This approach was used in the synthesis of the organosilicon dendrimers G₀-SiMe₂-C₆H₃(CH₂NMe₂)₂-1,3, G₀-SiMe₂-C₆H₄(CH₂NMe₂)₄, G₁-SiMe₂-C₆H₃(CH₂NMe₂)₂-1,3 and G₁-SiMe₂-C₆H₄(CH₂NMe₂)₄. The dendrimers synthesised and model compounds were metallated with Bu^tLi and further deuterated. Compound G₀-SiMe₂-C₆H₂(CH₂NMe₂)₂-1,3-Li-2 (**27**, X = Li) was converted into a platinum derivative under the action of 12 equiv. of PtCl₂(SEt)₂.

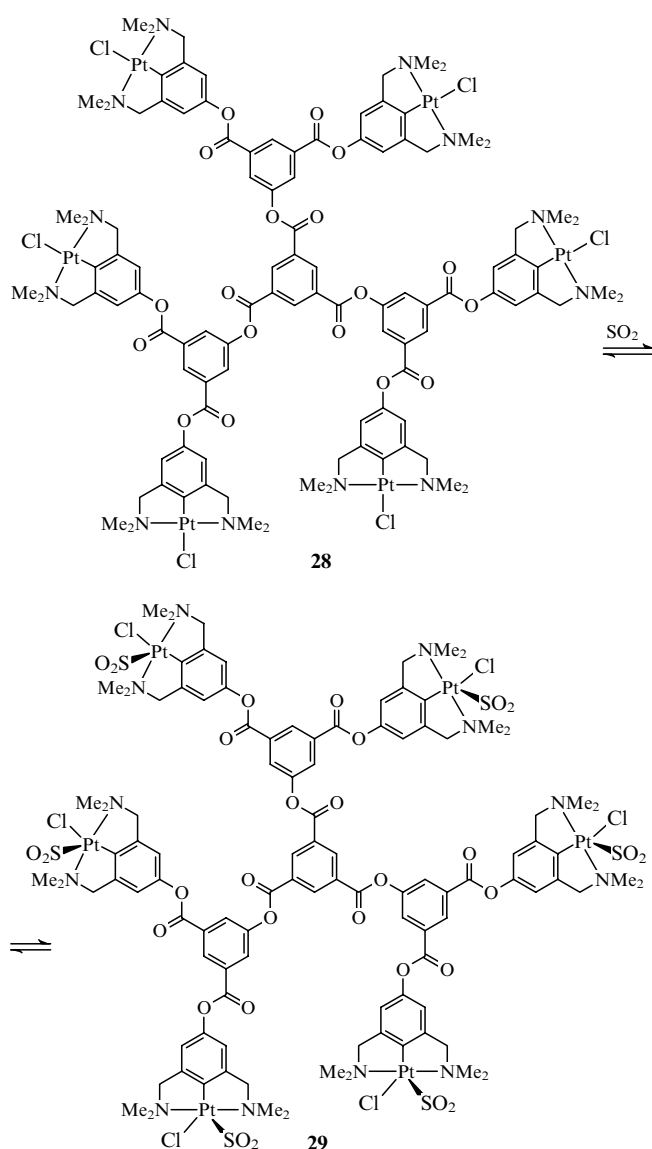


X = H, Li, D.

Catalytic activities of nickel complexes prepared on the basis of organosilicon dendrimers containing peripheral NCN pincer-type ligands were studied in the Kharasch-type addition of CCl₄ to alkenes.³² The kinetic data suggest that the catalytic activities of

zero- and first-generation dendrimers are lower than that of the monomeric catalyst (by 20% and 30%, respectively). However, complete separation of the catalyst from the reaction product by filtration through a membrane is an obvious advantage of dendrimers.³²

The dendrimer **28** containing cycloplatinated fragments with pincer groups was used as a sensor in the determination of SO₂.^{33,34} According to calculations, the molecule **28** is planar. In contrast with organosilicon dendrimers, this compound is poorly soluble in common organic solvents, which can be attributed to its structural peculiarities. Earlier studies have shown³³ that platinum and nickel complexes with NCN pincer ligands can reversibly bind SO₂; the resulting compound has the structure of a tetrahedral pyramid. The solubility of the complex formed is much higher than that of the starting compound. The dendrimer **28** (both in solution and in a solid state) reacts instantaneously with gaseous SO₂ to yield the corresponding addition products, which is accompanied by the appearance of an orange colour.



The formation of the adducts **29** was confirmed by ¹H NMR and UV spectroscopic data. The addition of SO₂ is reversible. The desorption of SO₂ occurs on heating of the adduct to 40 °C or *in vacuo*.

V. Dendrimers containing transition metal coordination complexes

1. Dendrimers containing coordination complexes with phosphine ligands

A search for novel catalytic systems stimulated the design of new ligands including those based on dendritic molecules with different electronic and spatial characteristics. It was anticipated that the use of dendritic ligands in combination with heterogenisation of a catalyst and biphasic systems would provide a clue to the problem of the catalyst's regeneration. Moreover, grafting of a catalyst on the surface of the dendrimer might enhance the regioselectivity by virtue of fixation of its conformation due to steric hindrances created by the dendrimer.³⁵ However, the experimental data available so far evidence that dendritic complexes manifest lower activities than their mononuclear analogues.³⁵ The reason for this may be related to steric hindrances and other problems due to larger sizes of dendrimers. Besides, the activity of a catalyst may be lost owing to the stabilisation of the complex by various functional groups present in the dendrimer.³⁵

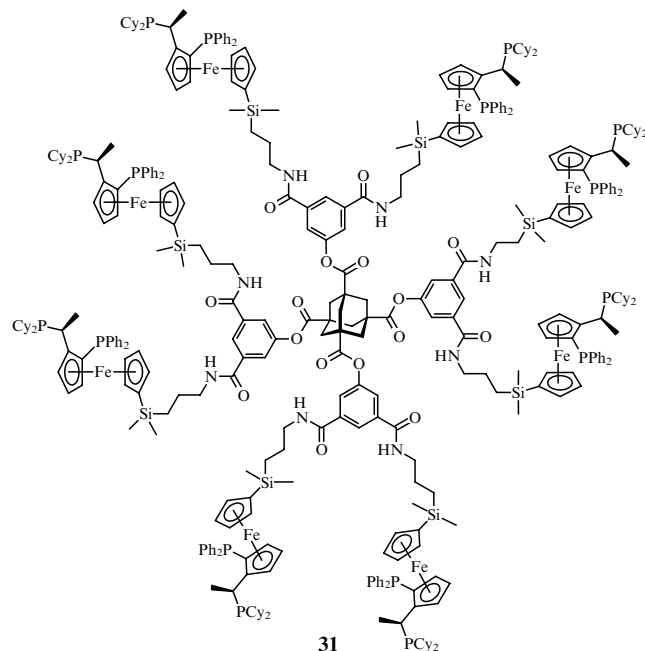
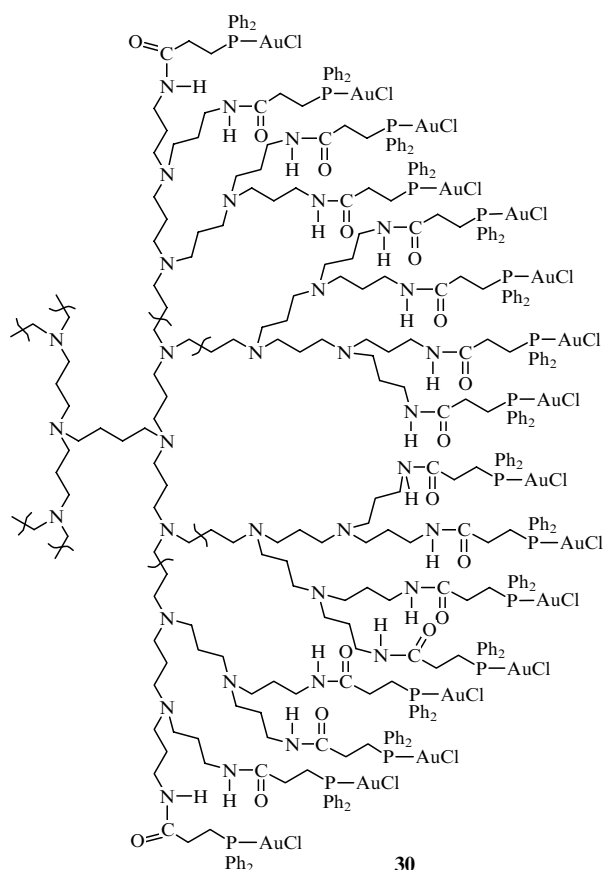
Tertiary phosphines can form complexes with virtually all transition metals; many of those efficiently catalyse various reactions. It is not surprising therefore that the overwhelming majority of publications are devoted to the dendrimers containing phosphine complexes of transition metals. Thus the synthesis of ruthenium complexes with phosphine-containing dendritic ligands was described and their catalytic activity was investigated.³⁵ However, reactivities of these dendritic complexes appeared to be lower than that of the original mononuclear complexes RuH₂(PPh₃)₄. Unlike the latter, dendrimers did not react with chloroform and formed insoluble compounds with alkenes which could not be characterised; these compounds slowly reacted with CO to give the corresponding carbonyls. Preliminary studies showed that dendritic ruthenium complexes displayed high catalytic activities in the hydrogenation of ketones.³⁵

Synthesis of dendrimers containing bidentate phosphine ligands [–CH=NN(CH₂PPh₂)₂] at the periphery and the preparation of platinum, palladium and rhodium complexes based on them have been described.³⁶ Dendritic platinum and palladium complexes were methylated in the reaction with MeMgBr and carbonylated by treatment with CO.

Dendritic polyamines containing terminal diphenylalkylphosphine groups, which are ideal ligands for the complexation with transition metals in lower oxidation states, have been synthesised.^{37,38} The structure of one such compound (its right half is shown), *viz.*, a multinuclear gold(I) complex with a fourth-generation dendrimer containing 32 terminal diphenylphosphine groups (complex **30**), is given below.³⁷

X-Ray diffraction analysis of analogous gold(I) mono- and binuclear complexes revealed the presence of intermolecular NH...O hydrogen bonds in their crystal structures. It was suggested that similar intramolecular hydrogen bonds are also present in the Au complex with dendritic ligands. Such gold(I) multinuclear complexes represent a new class of metal-containing polymers with definite, probably spheric structures with dendritic molecules as the supporting matrices. These complexes can be used as catalysts and in medicine for biochemical diagnostics and as anti-inflammatory and anti-tumour drugs.³⁷

Dendritic molecules containing chiral ferrocenyl phosphine ligands present special interest. Zero- (compound **31**) and first-generation dendrimers containing up to eight chiral diphosphine ligands were synthesised on the basis of benzene-1,3,5-tricarbonyl chloride and adamantane-1,3,5,7-tetracarbonyl chloride³⁹ and a silylated ferrocenyldiphosphine derivative [C₅H₃(PPh₂)(CHMe.₂PCy₂)]Fe(C₅H₄SiMe₂CH₂CH₂CH₂Cl), where Cy is cyclohexyl.

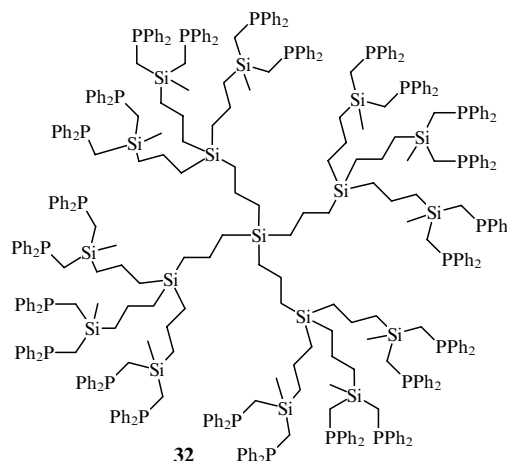


Catalytic properties of rhodium complexes prepared by the reaction of $[\text{Rh}(\text{COD})_2]\text{BF}_4$ (COD is cycloocta-1,5-diene) with these dendritic ligands were studied in asymmetric hydrogenation of dimethyl itaconate. An enantiomer of dimethyl 2-methylbutane-1,4-diolate was obtained with *ee* 98%, which is only 1% lower than that achieved with a mononuclear complex.[‡] This

[‡] Mononuclear catalysts (ferrocene derivatives) are used in the commercial production of pesticides.⁴⁰

result is remarkable in that in this case the catalyst can be fully separated from the reaction products using membrane technology.

Dendrimers of the type **32** with peripheral diphenylphosphinomethyl ligands were synthesised from the organosilicon dendrimers $\text{G}_x-\text{CH}_2\text{CH}_2\text{SiMeCl}_2$ ($x = 0, 1$) by reacting them with $\text{Ph}_2\text{PCH}_2\text{Li} \cdot \text{TMEDA}$ (TMEDA is *N,N,N',N'*-tetramethylethylenediamine).⁴¹



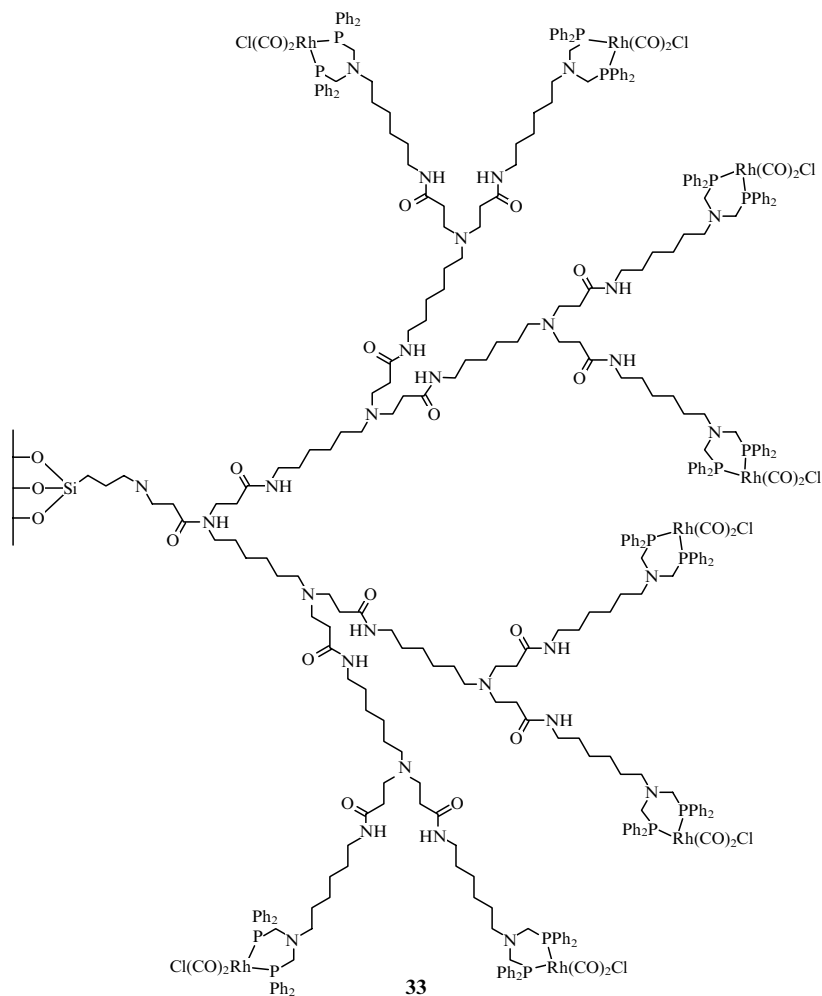
The reaction of $[(\eta^3-\text{C}_3\text{H}_5)\text{PdCl}]_2$ with the dendrimer **32** afforded a palladium complex which was further used as a catalyst in the allylic alkylation of diethyl methylmalonate with sodium allyltrifluoroacetate in both a batch process and in continuous process using a membrane reactor. In the former case, the catalyst manifested an exceedingly high activity. The yield of the reaction product exceeded 80% after 30 min at a substrate : catalyst ratio of 2000 : 1 (see §). However, in a continuous membrane reactor at the same ratio of the reactants, the initially high catalytic activity was gradually almost extinguished following passage of 15 reactor volumes of the reaction mixture. The reaction mixture at the outlet from the reactor did not contain any catalyst. This loss of the catalytic activity was attributed to the decomposition of the palladium complex.

Synthesis of silica gel-grafted polyamidoamine dendrimers containing peripheral diphenylphosphinomethyl groups has been carried out.^{42,43} These dendrimers were used to prepare the corresponding rhodium complexes **33** which present interest as recyclisable catalysts in the reaction of alkene hydroformylation and can be used, in particular, in the production of drugs of the ibuprofen and naproxen type.⁴² Studies of the catalytic activities of such dendritic catalysts revealed that these activities increased with the increase in the length of the carbon chain between the amide and amine nitrogen atoms from two to six carbon atoms and did not change further. Such an increase in the catalytic activity seems to be due to the reduction of steric hindrances on the surface of the dendrimer.

Hydroformylation of styrene and vinyl acetate involving such catalysts occurred with virtually quantitative yields and high regioselectivity. The catalysts retained high catalytic activities over at least four cycles. However, slow wash-out[¶] of rhodium from the dendrimer immobilised on silica gel did occur.

§ With respect to 1 mol of the catalytically active groups.

¶ It is noteworthy that rhodium is not washed out from the catalyst with a pure solvent, but is washed out in the presence of CO or a $\text{CO}-\text{H}_2$ mixture, apparently, as a result of exchange of dendritic phosphine ligands in the rhodium complexes for CO.



2. Dendrimers based on metal complexes with polypyridine ligands

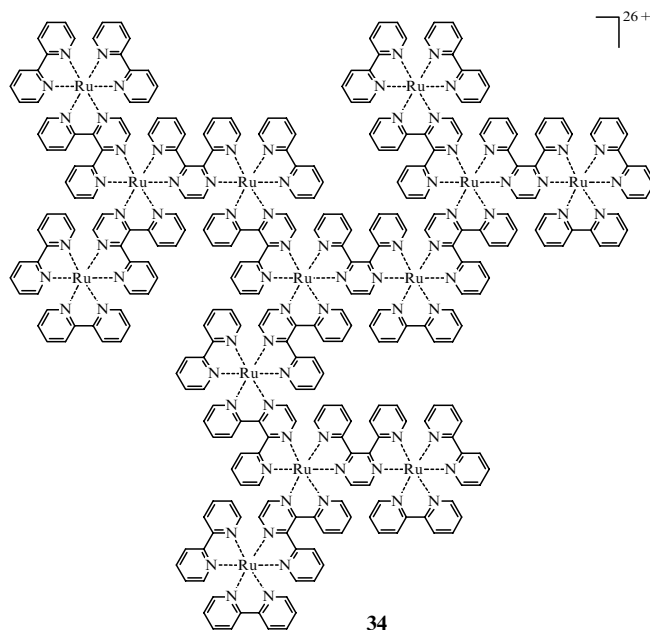
In the foregoing section we considered the methodology of synthesis of metal-containing dendrimers based on the formation of new carbon–carbon or carbon-heteroatom bonds. Coordination of polydentate organic ligands around metal atoms is an alternative route to the construction of metal-containing dendrimers.⁴⁴ This procedure was used, in particular, in the synthesis of the dendrimer **34** containing ruthenium cations coordinated by 2,3-bis(2-pyridyl)pyrazine.⁴⁴

In such dendrimers, transition metal coordination complexes function both as branching and linking blocks. These dendrimers are prepared using the ‘complex-as-a-metal–complex-as-a-ligand’ synthetic strategy in which a complex with free chelating groups (‘complex-as-a-ligand’) chelates a complex with labile ligands (‘complex-as-a-metal’). This approach allows stepwise monitoring over the dendrimer growth and involvement of building blocks containing various metals or ligands at each stage of the synthesis.

Dendrimers comprising complexes of different chemical nature can possess specific chemical properties, *e.g.*, provide gradients for electron transfer. Because of their remarkable photophysical and electrochemical properties, ruthenium(II) and osmium(II) complexes with polypyridine ligands represent ideal components for the synthesis of luminescent materials and other materials which can transform the light energy.⁴⁴

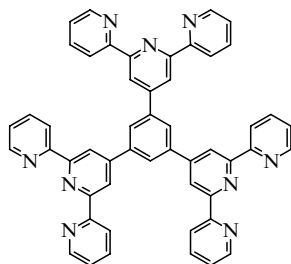
Numerous dendritic compounds were synthesised based on 2,3- and 2,5-bis(2-pyridyl)pyrazine (2,3- and 2,5-dpp) as the connecting ligands and 2,2'-bipyridine (bipy) as the terminal

ligand.⁴⁴ These complexes contain several chromophore groups and a large number of redox centres.



34

2,2':6',2''-Terpyridine (terpy) and its derivatives were used as ligands in the synthesis of metal-containing fragments of dendrimers. The synthesis of 1,3,5-tris(2,2':6',2''-terpyridin-4'-yl)benzene,

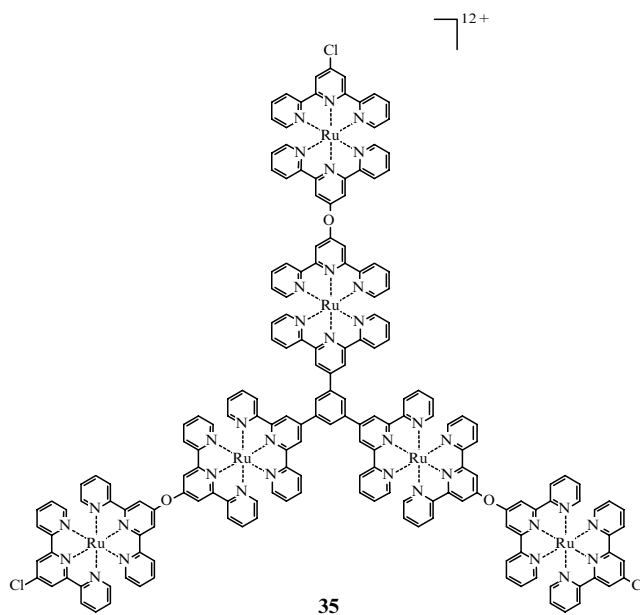


trinuclear⁴⁵ and hexanuclear (**35**)⁴⁶ ruthenium complexes prepared on its basis has been described.⁴⁵

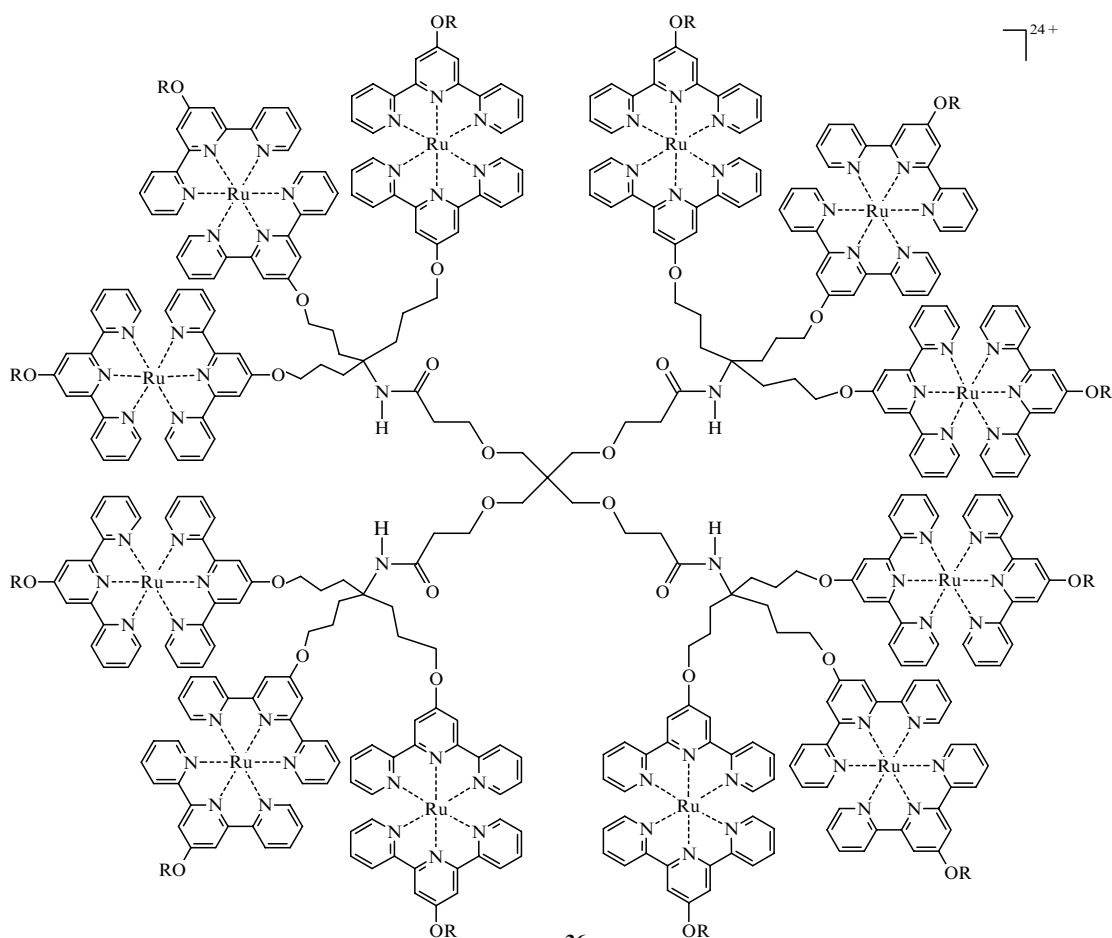
The dendritic complex **36** containing 12 ruthenium atoms was obtained by a reaction of 12 equiv. of (terpy)RuCl₃ with a polyamide-based dendritic ligand.⁴⁷

The reaction of 1 equiv. of 1,3,5-tribromomethyl-2,4,6-trimethylbenzene with 3 equiv. of the ruthenium complex **37** was used to prepare the dendritic complex **38** containing six ruthenium atoms (Scheme 2).⁴⁸

A similar reaction of 1 equiv. of hexabromomethylbenzene with 6 equiv. of compound **39** gave the dendritic complex **40** containing 18 ruthenium atoms (Scheme 3).⁴⁹ Studies of electro-

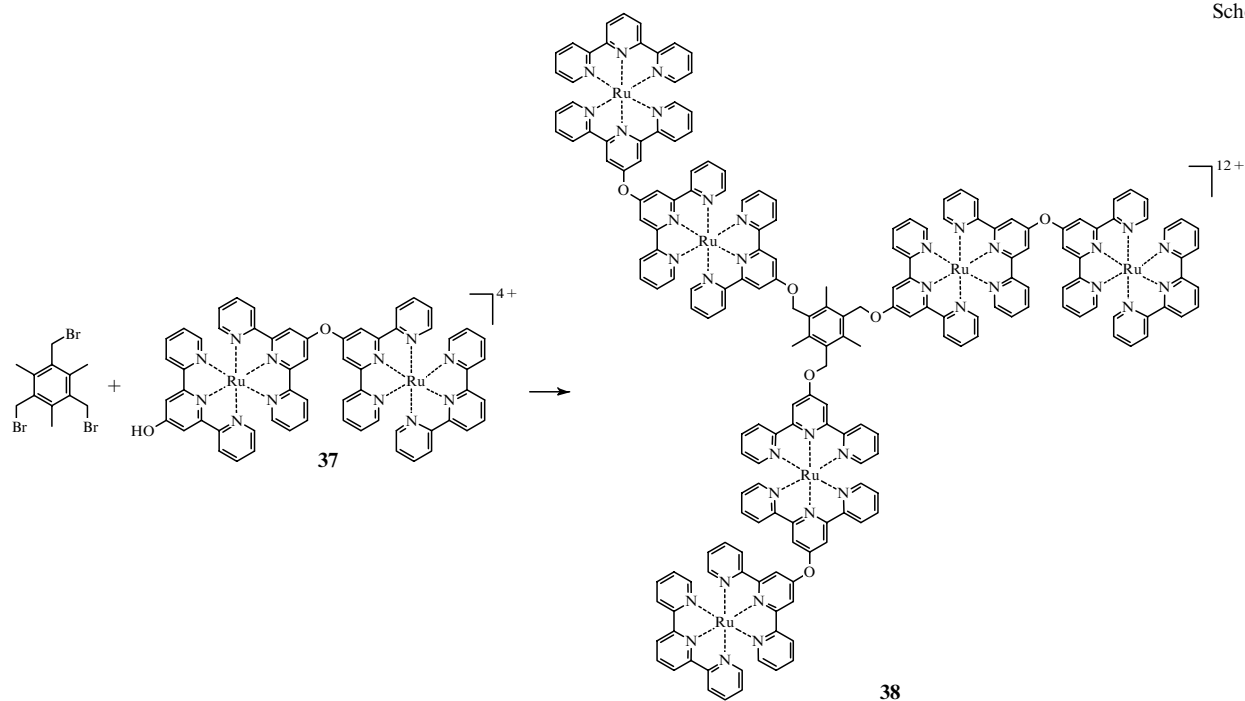


chemical properties of compound **40** revealed that all ruthenium centres are independent and do not apparently interact with one another.

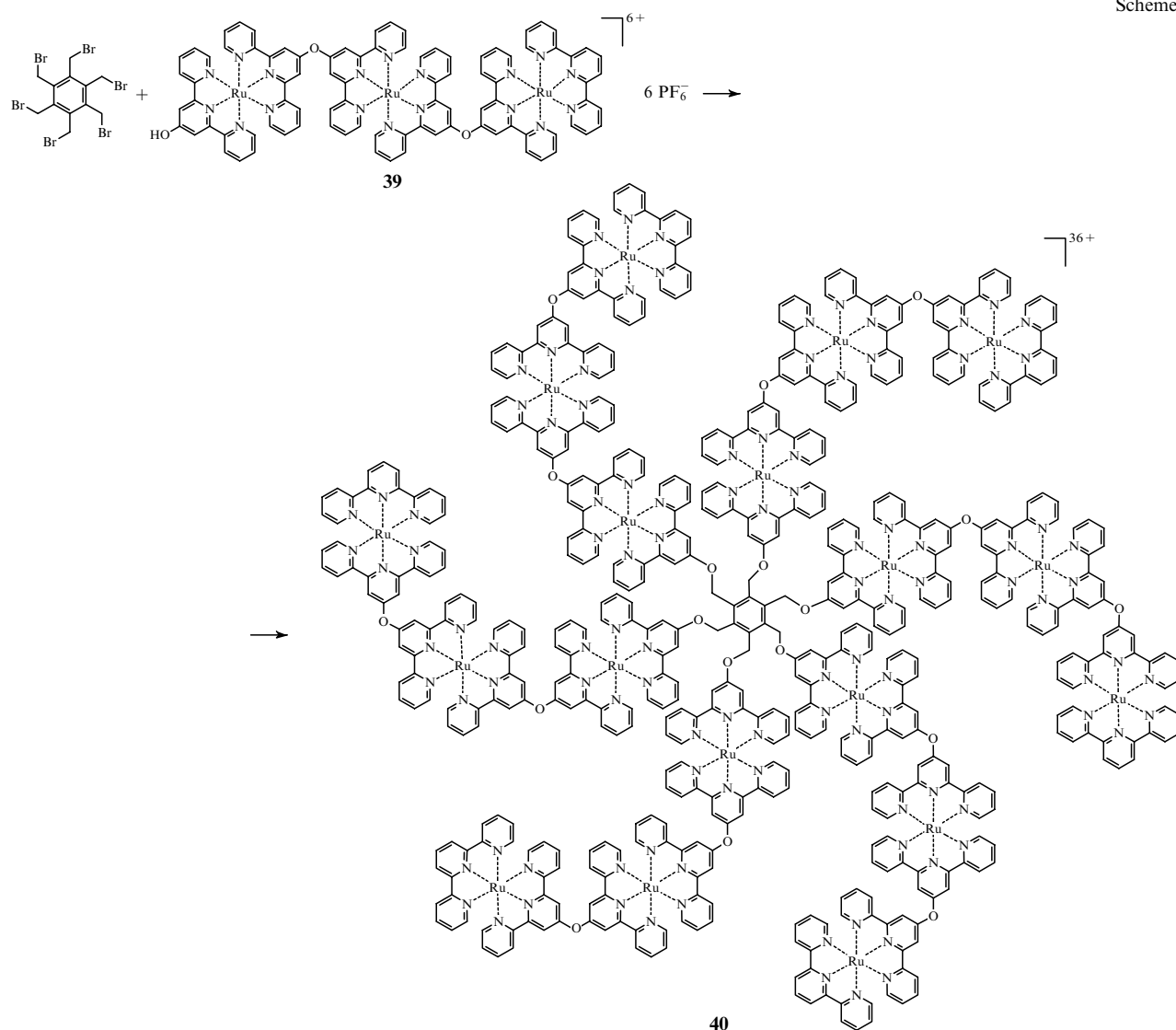


R = (CH₂)₃C[(CH₂)₃OBn].

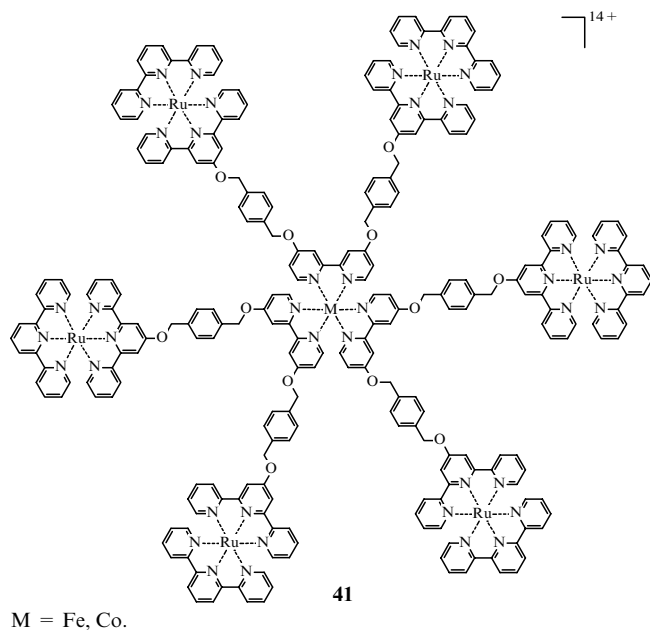
Scheme 2



Scheme 3



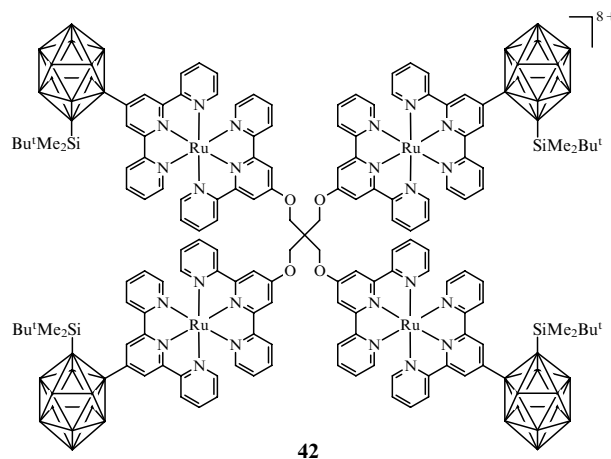
The dendrimers **41** containing ruthenium atoms at the periphery and iron or cobalt atoms in the core were prepared on the basis of polypyridine ligands.⁵⁰



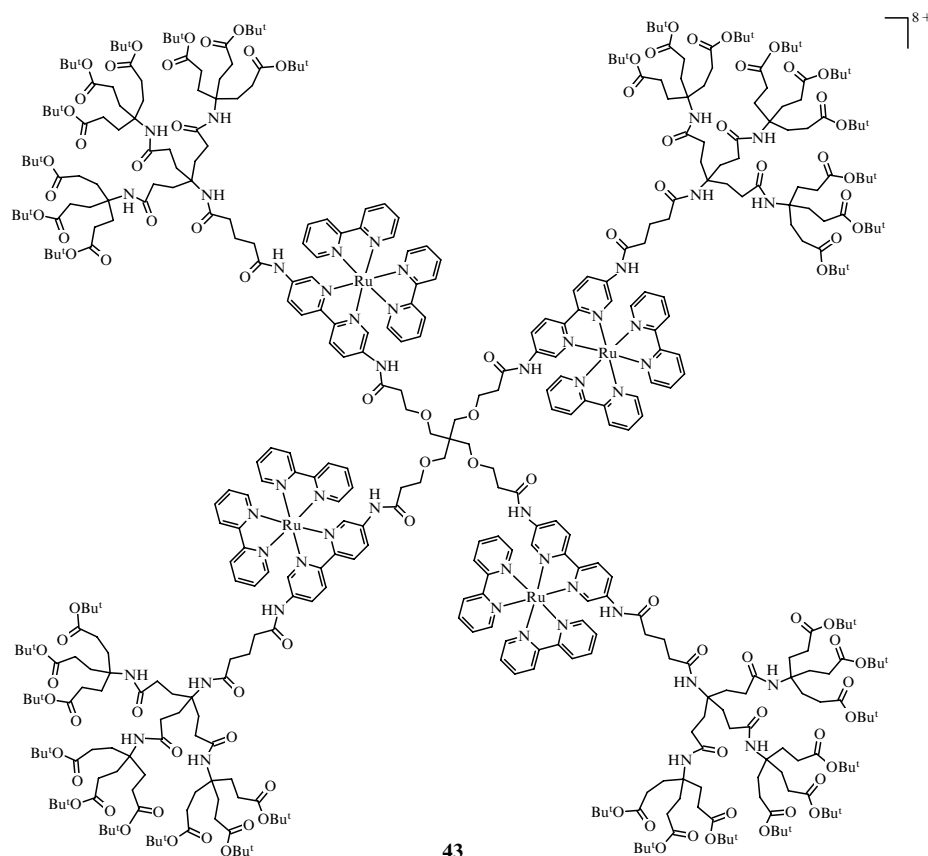
The central fragment of the dendrimer **41** was synthesised by complexation of a substituted bipyridine ligand to iron(II) or cobalt(II) ions.⁵⁰ The complex formed was introduced into reaction with a terpyridine ruthenium complex. Studies of electrochemical properties of the dendrimers revealed that a reversible redox process $\text{Ru(II)} \rightleftharpoons \text{Ru(III)}$ can occur at +0.81 V; however,

no apparent redox reaction involving iron or cobalt ions in the dendrimer core could be detected.⁵⁰

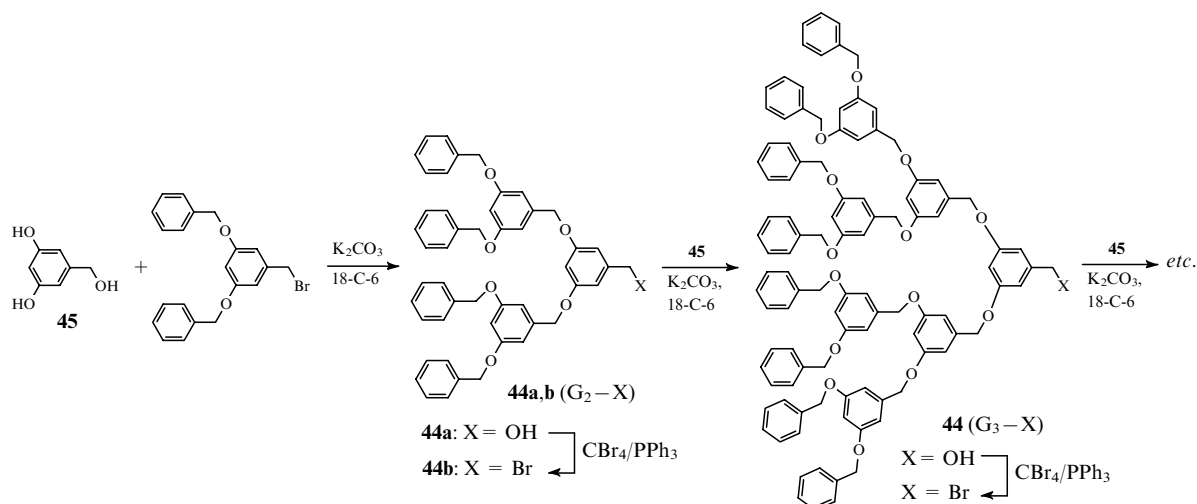
The incorporation of four bulky carborane groups at the periphery of the pentaerythritol-based ruthenium-containing dendrimer (complex **42**)⁵¹ resulted in restrictions of the conformational mobility, which was confirmed by magnetic non-equivalence of four methylene groups in the core and of two methyl groups at the periphery of the dendrimer. This had no effect on the electrochemical characteristics of the polypyridine ruthenium complexes of the type **42**.



The dendrimer **43** containing four ruthenium complexes with bipyridine ligands has been described.⁵² The NMR spectra of this dendrimer are extremely complex; therefore, its structure was established on the basis of UV spectroscopy, MALDI-TOF mass spectrometry and cyclic voltammetry.



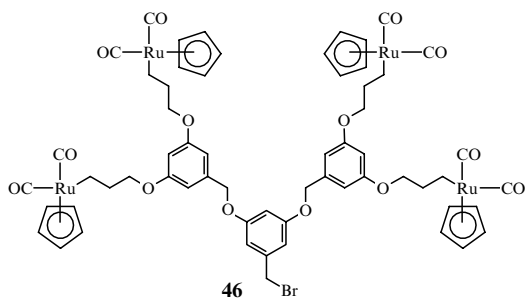
Scheme 4



VI. Dendrimers containing complexes with metal – carbon σ -bonds

The convergent approach was used⁵³ in the synthesis of the dendrimers **44** with 3,5-dibenzoyloxybenzyl groups at the periphery (Scheme 4). 3,5-Dihydroxybenzyl alcohol (**45**) has been used as the monomer. It was noted⁵⁴ that the advantage of the convergent strategy is that it allows accurate monitoring of the number and localisation of functional groups in the final product. The intermediate products were isolated, purified and characterised after each step. Since all the intermediate and final products are easily soluble, the course of the reaction was monitored by NMR spectroscopy. Thus, any potential defects which might occur in the synthesis of dendrons could be detected prior to their attachment to the central fragment of the dendrimer.

The organoruthenium compounds of the type **46** were synthesised in a similar fashion.⁵⁴ The resulting metal-containing dendrimers were rather stable, which made it possible to synthesise larger dendritic structures containing Ru – C π - and σ -bonds.

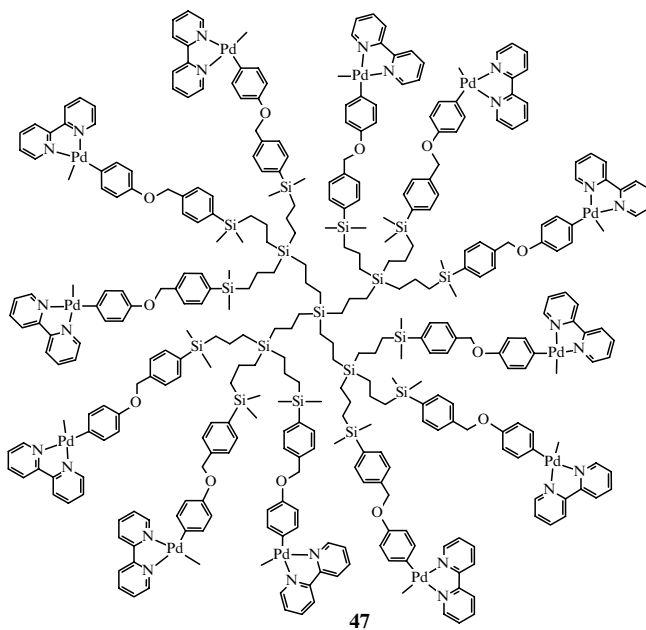


This approach was used in the synthesis of third- and fourth-generation dendrimers containing up to 48 ruthenium atoms.⁵⁴ All the organoruthenium compounds thus prepared are readily soluble in common organic solvents.

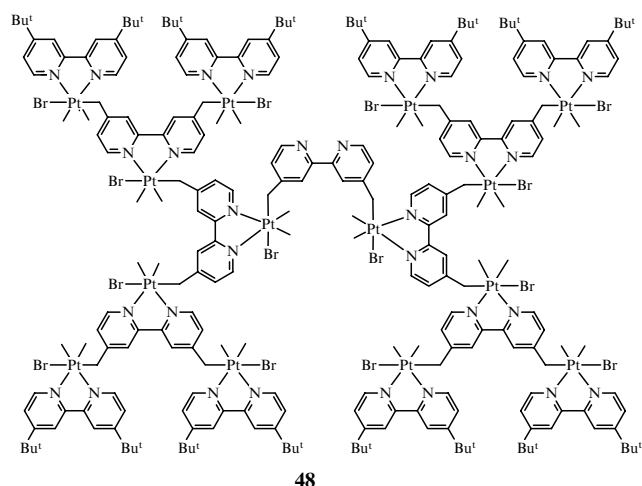
A first-generation organosilicon dendrimer containing 12 peripheral organopalladium units was synthesised by oxidative coupling of the $[Pd_2(dba)_3 \cdot dba/TMEDA]$ complex (dba is dibenzylidenacetone) to a dendrimer containing iodoarene groups. Further reaction of the metal-containing dendrimer with MeLi and bipyridine⁵⁵ resulted in the dendrimer **47**.

The oxidative addition of benzyl bromide to the Pd-containing dendrimer **47** was studied. The stability of the newly formed

dendrimer containing organic derivatives of Pd(IV) and the main pathways of its decomposition were determined.



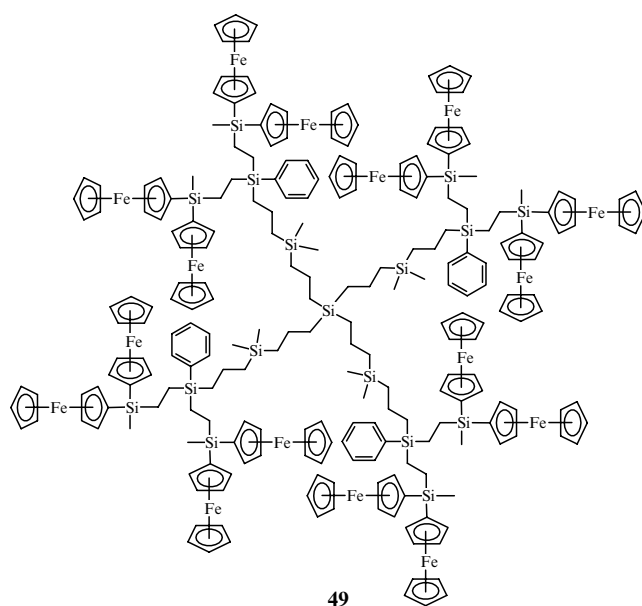
The synthesis of organoplatinum dendrimers of the type **48** has been described.⁵⁶ This involved the attachment of benzyl halides (RX) to $[PtMe_2(NN)]$ (where NN is the diimine ligand, *e.g.*, 2,2'-bipyridine). The reaction occurs with quantitative yields; however, the synthesis of larger dendrimers is complicated, since the solubility of the reaction products decreases as the size of the molecule increases. This reaction was followed by a colour change from orange-red (Pt^{II} complexes) to pale yellow (Pt^{IV} complexes). The increase in the chain length was repeated until NMR spectroscopy showed that the products contained structural defects. Larger organoplatinum dendrimers were obtained if the ligands were modified by introduction of *tert*-butyl groups, which increased the solubility of the dendrimers.⁵⁷ This synthesis employed a convergent strategy. The $[Pt^{IV}Me_4(\mu-SMe_2)_2]$ complex and 4,4'-bis(bromomethyl)-2,2'-bipyridine were used as the monomer units. The dendrimer **48** containing 14 platinum atoms was the last member of the series that has been synthesised. An attempt at preparing a dendrimer of the next generation containing 30 platinum atoms failed.



More recent studies⁵⁸ were aimed at investigating the possibility of synthesising multinuclear organopalladium compounds and bimetallic palladium–platinum dendrimers by the convergent approach. These studies showed that in this case the use of organopalladium compounds is limited because of the tendency of palladium(IV) complexes to undergo a reverse reaction, *viz.*, to the reductive elimination of alkyl halide.

VII. Dendrimers containing terminal ferrocenyl groups

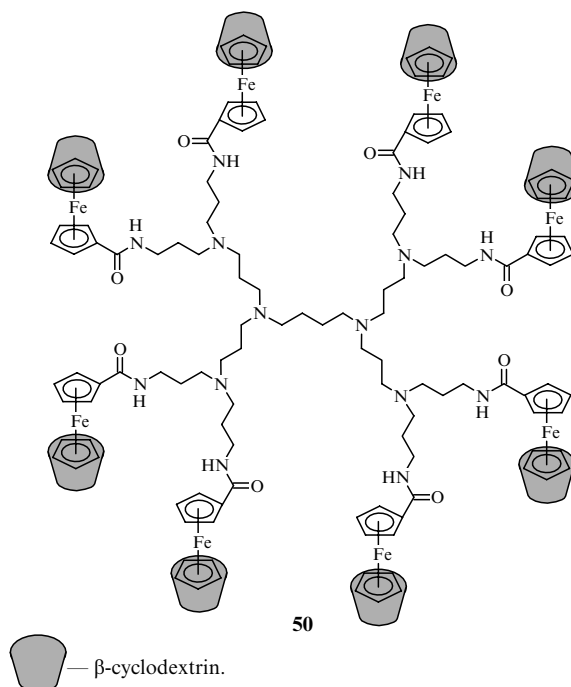
The majority of iron-containing dendrimers reported so far contain iron in the form of ferrocenyl groups. This can be explained by the fact that the chemistry of ferrocenes is well-studied and its derivatives are rather stable compounds. The synthesis of such systems aimed at the construction of dendrimers which could undergo redox reactions involving electron interactions between the metal-containing fragments.⁵⁹ The electronic interaction between the transition metal atoms within one of such dendrimers (**49**) has been studied; its structure is shown below.



Polymers containing ferrocene derivatives are currently used for modification of electrodes and redox catalysts and biosensors.⁶⁰ The cation $[\text{FeCp}(\text{arene})]^+$ can be used as a starting material in the synthesis of dendrimers by the polyalkylation reaction. $[\text{FeCp}(\text{C}_6\text{Me}_6)]\text{PF}_6$ reacts with an excess of a base and ferrocenylalkyl halide $\text{I}(\text{CH}_2)_4\text{Fc}$ (Fc is $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4$) resulting in

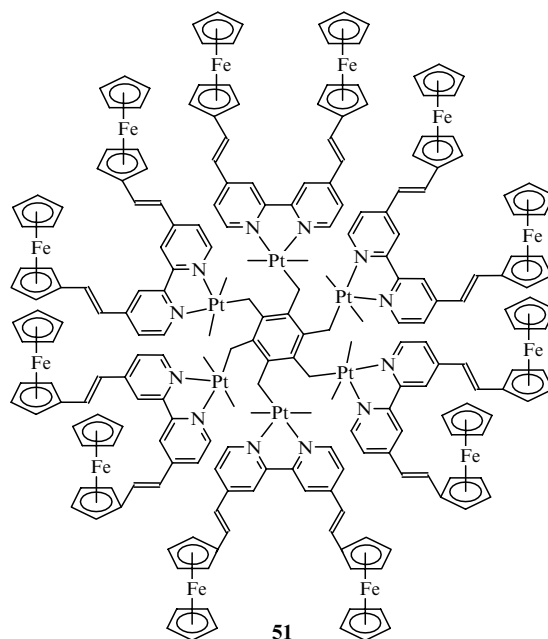
selective hexasubstitution to give $\{\text{FeCp}[\text{C}_6(\text{CH}_2)_5\text{Fc}]_6\}\text{PF}_6$. According to cyclic voltammetry data, all the six ferrocenyl groups are electrochemically equivalent, being oxidised at the same potential. The positive charge in the central fragment of the molecule has no effect on the oxidation process.⁶⁰

The dendrimer containing peripheral ferrocenyl groups can form inclusion compounds with cyclodextrins (see, *e.g.*, compound **50**)⁶¹ localised at its periphery where they form a supramolecular structure of an even greater size.



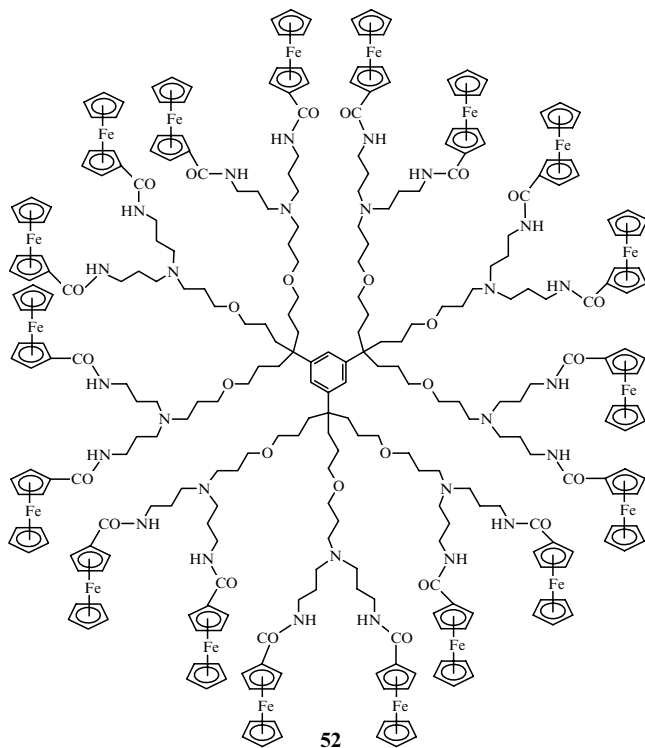
The number of ferrocenyl groups incorporated into cyclodextrin molecules is limited by steric hindrances on the surface of the dendrimer. In the case of the dendrimer **50**, the reaction between the ferrocenyl groups and cyclodextrin is complete.

The synthesis of an unusual dendritic molecule **51**, which simultaneously incorporates Fe and Pt atoms (the platinum fragments in the centre and the ferrocenyl groups at the periphery), has been described.⁶²



In this case, the dendritic molecule was assembled from fragments containing one platinum atom and two ferrocenyl units, which were attached to the central fragment, *viz.*, hexakis(bromomethyl)benzene. This dendrimer was characterised by electrochemical and spectroscopic methods.

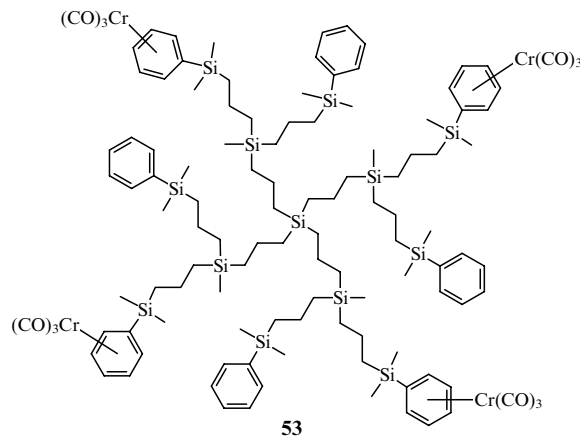
Dendrimers of the type **52** containing peripheral ferrocenyl groups linked to the central fragment through the amide groups have been used as sensors in the determination of inorganic anions (Cl^- , NO_3^- and HSO_4^- , see Ref. 63). Cyclic voltammograms of such dendrimers have the forms of simple reversible waves, which suggests that all of the ferrocenyl groups are equivalent in the oxidation process of Fe(II)/Fe(III) .⁶³ In this case, the 'sensitivity' of the dendrimers to the nature of the anion in the redox process increases on going from zero- (G_0) to the first-generation dendrimers (G_1), reaching a maximum for a second-generation dendrimer (G_2) preceding the third-generation dendrimer (G_3) where steric saturation of the surface with the ferrocenyl groups takes place. With an increase in the generation number, the ferrocenyl groups on the surface of the dendrimer become more closely spaced; this results in a decrease in the sizes of the cavities where the anions could penetrate.



An optimal dendrimer for smaller anions is that belonging to a generation in which the number of ferrocenyl groups precedes steric saturation of the surface, which ensures the most suitable bulk of the cavities.⁶³

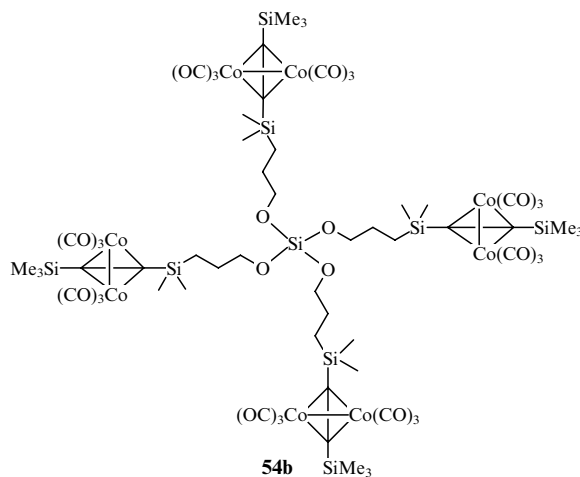
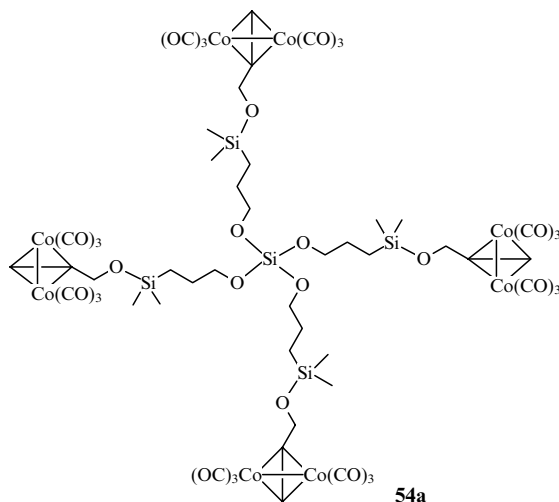
VIII. Dendrimers containing transition metal π -complexes

One of the ways of modification of dendrimers containing arene groups at the periphery consists in the formation of π -arene complexes of transition metals. Thus, the synthesis of first- and second-generation organosilicon dendrimers (*e.g.*, the dendrimer **53**) containing aromatic rings with the Cr(CO)_3 groups linked has been described.⁶⁴

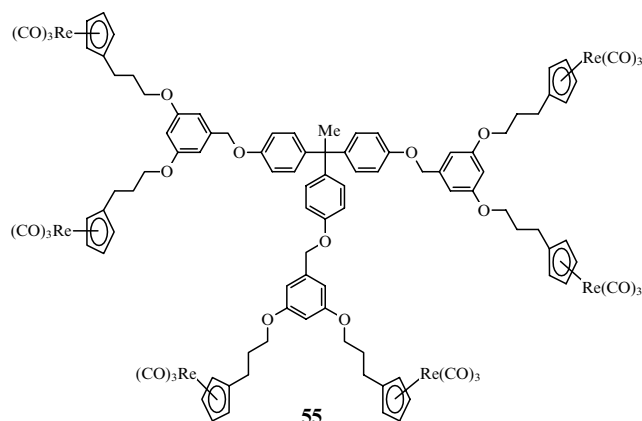


The starting organosilicon dendrimer was obtained by stepwise hydrosilylation and allylation. To this end, tetravinylsilane was introduced into the hydrosilylation reaction with methyl-dichlorosilane; the product formed was allylated with allylmagnesium bromide and repeatedly hydrosilylated with phenyldimethylsilane. The complexation involved only four out of eight benzene rings. The attempts to prepare a dendrimer with eight chromium atoms failed, since this required more drastic reaction conditions which resulted in the decomposition of the dendrimer.

Some first-generation organosilicon dendrimers containing peripheral alkyne groups further converted into the cluster π -complexes **54a** and **54b** by a reaction with $\text{Co}_2(\text{CO})_8$ have recently been synthesised.⁶⁵



The organometallic dendrimer **55** containing six peripheral rhenium atoms was synthesised from the 3,5-dihydroxybenzyl alcohol using the convergent approach.⁶⁶

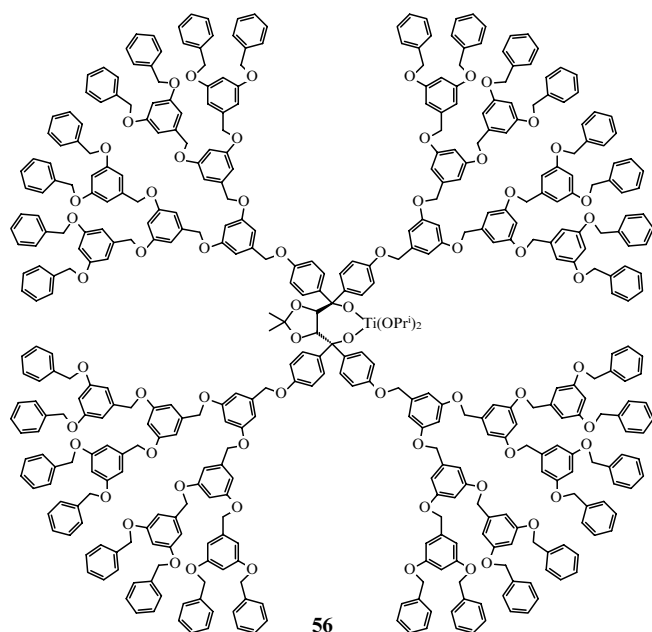


However, an attempt at using this compound as a starting material for the synthesis of a dendritic oxo-rhenium complex by conversion of the carbonyl groups, which could be used as a catalyst in oxidation reactions, was unsuccessful.

IX. Dendrimers containing central metal-containing fragments

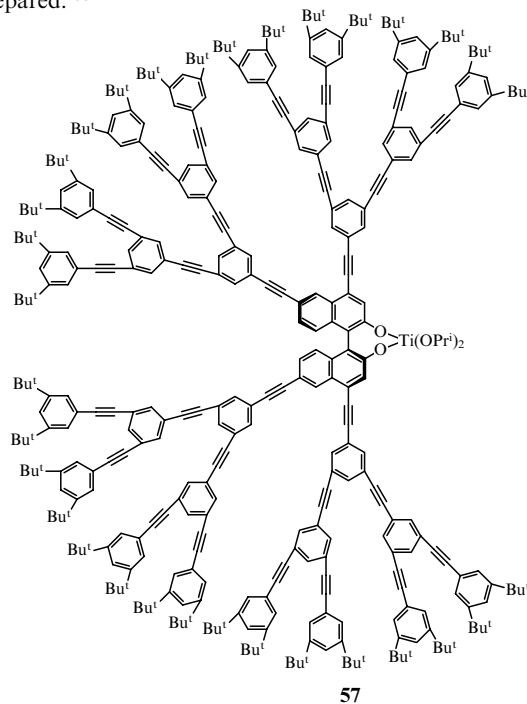
The syntheses of dendrimers containing chiral titanium complexes in the centre of the molecule have recently been reported.^{67,68} In these studies, (*R,R*)- $\alpha,\alpha',\alpha',\alpha'$ -tetraaryl-1,3-dioxolane-4,5-dimethanol (TADDOL) has been used as the core to which four dendrons prepared on the basis of 3,5-dihydroxybenzyl and/or octyl fragments were attached by the benzylation reaction.⁶⁷

The catalytic activity of titanium complexes of the type **56** was studied in addition of diethylzinc to benzaldehyde. A slight



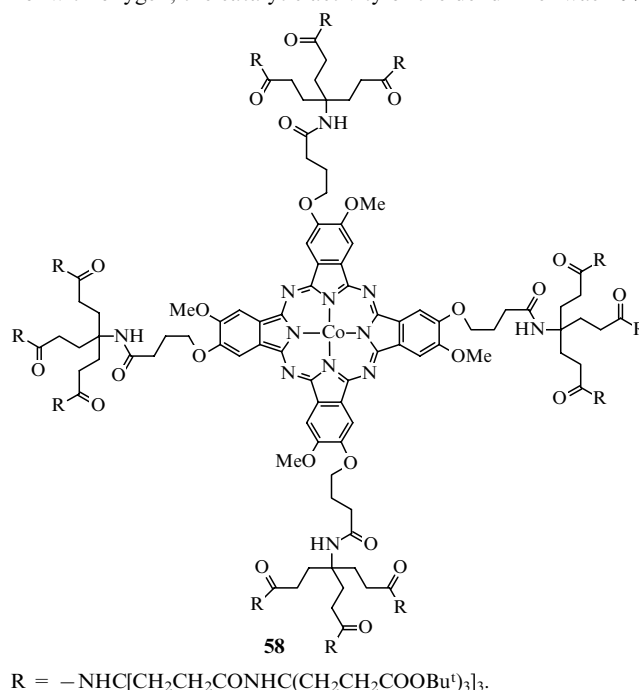
decrease in the catalytic activity and stereoselectivity with the increase in the number of dendrimer generations from zero to third was observed. However, on going to the fourth-generation dendrimers the decrease in the catalytic activity was more pronounced, being nearly two-fold. These results leave hope that second- and third-generation dendrimers can have possible applications as catalysts in membrane reactors.

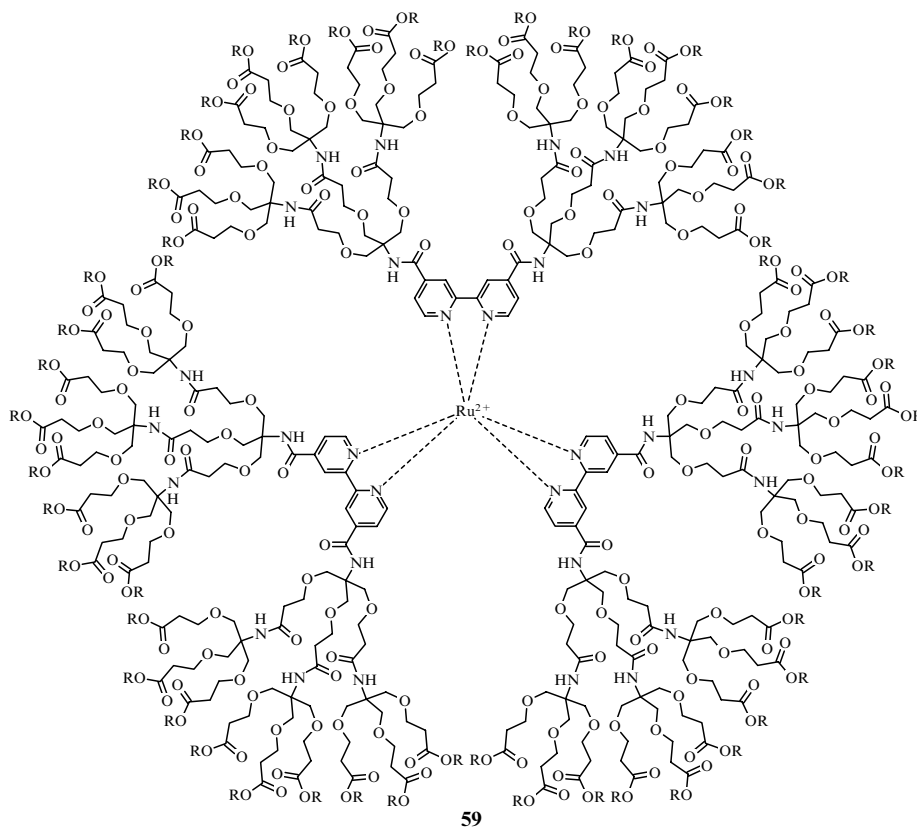
Analogously, dendrimers based on 1,3,5-triethynylbenzene with a central optically active 1,1'-bis(2-naphthol) fragment were prepared.⁶⁸



These dendrimers present special interest as chiral ligands and are used to recognise enantiomers. Catalytic activity of the titanium complex **57** was studied in the addition of diethylzinc to aldehydes, the enantiomeric excess attained being 89%–90%. Yet another possible application of these dendrimers is the construction of a fluorescent probe for optical determinations of enantiomeric compositions of chiral compounds.

A dendrimer containing phthalocyanine as the central fragment and its cobalt complex **58** have been described.⁶⁹ Studies of the electrochemical properties of the dendrimer **58** showed that the dendritic shell prevents intermolecular interactions of the phthalocyanine fragments and thus impedes the electron transfer to the centre of the molecule. In the oxidation of 2-mercaptoethanol with oxygen, the catalytic activity of the dendrimer was 20%



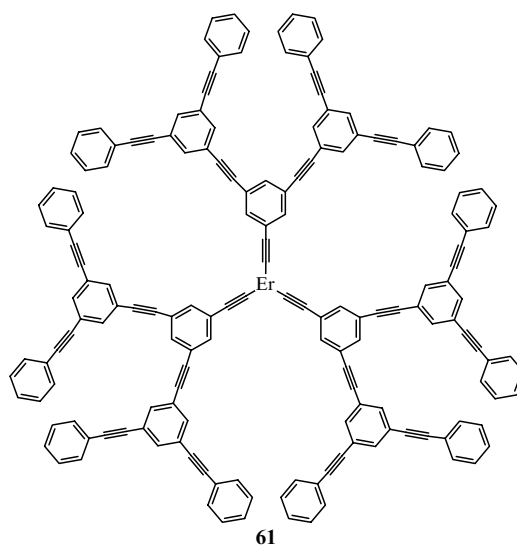
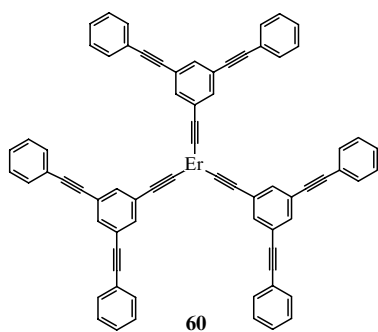


lower than that of the analogous non-dendritic phthalocyanine catalyst but its stability was higher in comparison with the latter.

A great number of papers are devoted to the synthesis of dendrimers containing metal-porphyrin complexes as the central fragments. Such compounds present interest as selective oxidation catalysts mimicking enzymes.⁷⁰ The dendritic shell enhances the regioselectivity of the catalyst thus increasing its similarity to enzymes. In addition, such compounds were used in model studies of electron transfer in biological objects⁷¹ and as fluorescent probes.⁷²

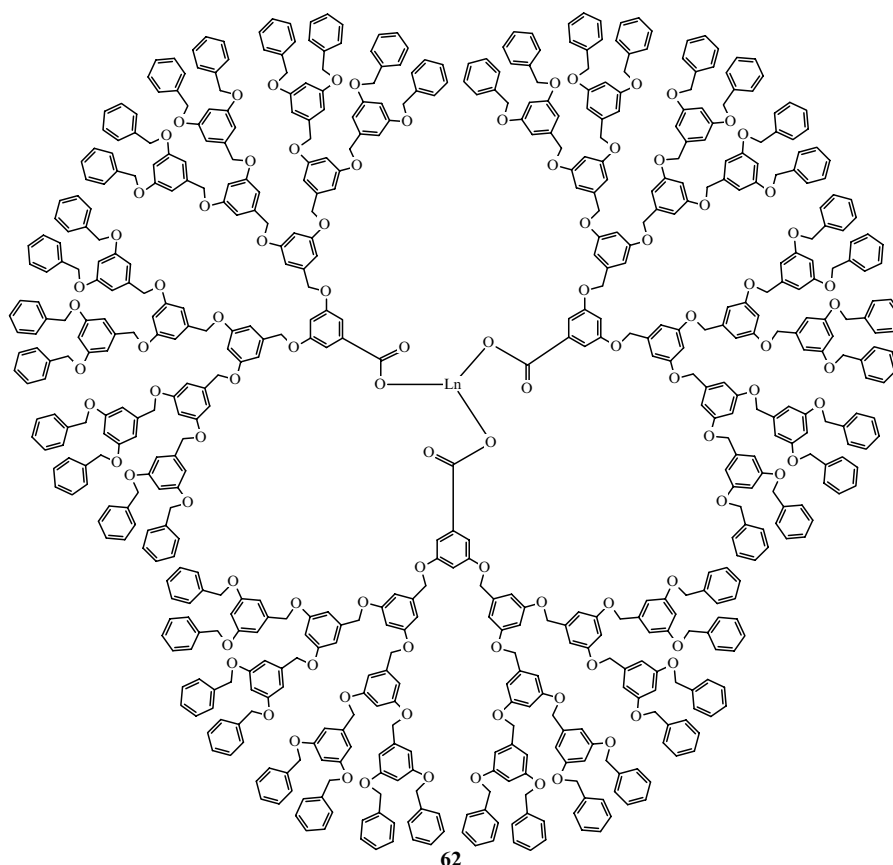
Yet another possible application of dendrimers is the use of their shells as protectors for the cores. The ruthenium(II) complex **59** coordinated to three dendritic bipyridyl ligands provides an example.⁷³ It was shown that the lifetime of this complex in the excited state exceeds that of its non-dendritic analogue, since the dendritic shell protects the central part of the dendritic molecule from contacts with a solvent and dissolved oxygen and thus prevents luminescence quenching.

The organoerbium dendrimers of the first (**60**) and second (**61**) generations⁷⁴ were synthesised in the reaction of $Er[N(SiMe_3)_2]_3$ with phenylethynyl dendrons.



The starting phenylethynyl dendrons of the first and second generations were synthesised by using the convergent approach developed earlier for phenylethynyl dendrons with peripheral 3,5-di-*tert*-butylphenyl groups.⁷⁵ According to the computer simulation data, phenylethynyl dendrons represent rigid planar molecules which apparently do not provide sufficient shielding of the central erbium atom despite their considerable sizes. For example, the dendrimers **60** and **61** synthesised are as sensitive to atmospheric oxygen and moisture as other compounds of the organo-lanthanide series.⁷⁴

Lanthanide derivatives are widely employed as lumino-phores.⁷⁶ However, the quantum yields of luminescence of lanthanide cations decrease as a result of cluster formation. In order to prevent luminescence quenching, lanthanide cations are encapsulated into a dendritic shell.^{76,77} To this end, lanthanide triace-

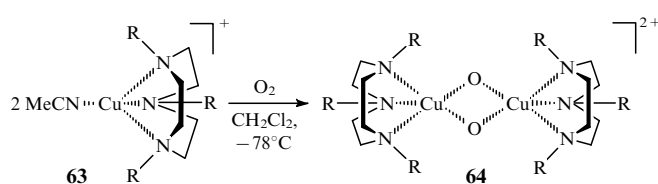


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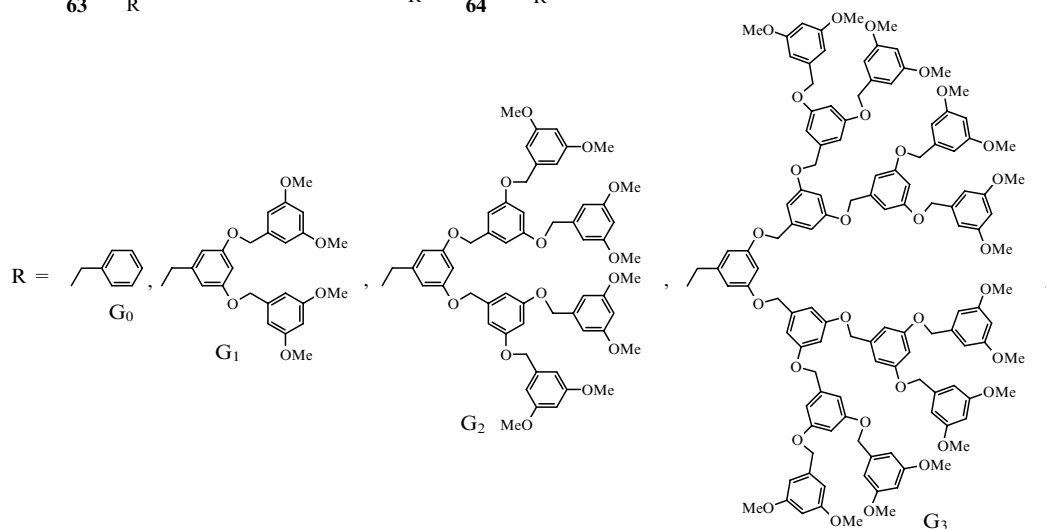
tates are introduced into a reaction with dendrons prepared on the basis of 3,5-dihydroxybenzyl fragments containing carboxy groups. The quantum yields of luminescence of the lanthanide complexes thus prepared (**62**) increased with the increase in the generation number for both solid samples and strongly diluted solutions of dendrimers in toluene. This effect can be attributed to the shielding of the lanthanide cations by dendritic ligands and the 'antenna effect', *i.e.*, the transfer of photoexcitation energy from the dendritic ligands to the lanthanide cations in the centre of the

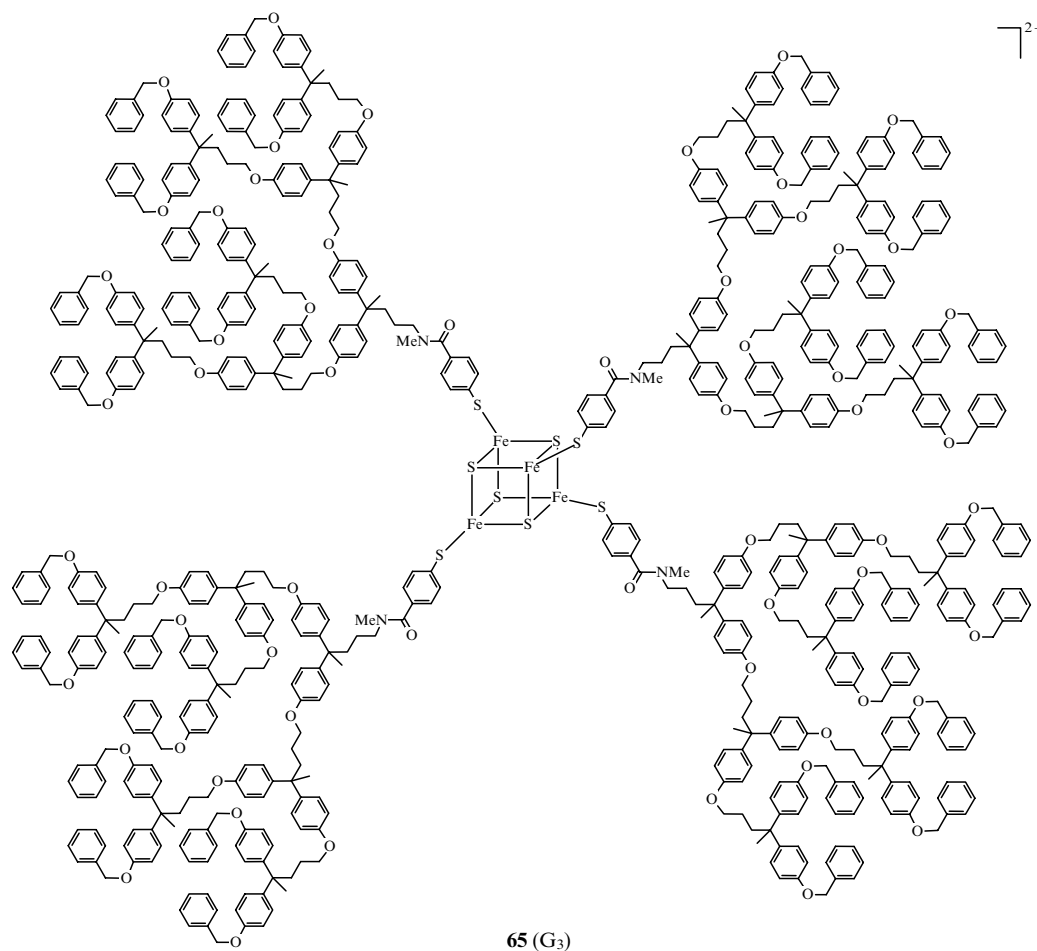
dendrimers despite the fact that dendrons based on 3,5-dihydroxybenzyl halides are not conjugated molecules.

Synthesis of a series of dendrimers of the first, second and third generations the nuclei of which represent monovalent copper complexes with 1,4,7-triazacyclononane have been described.⁷⁸ The rate constants for the oxidation of the dendritic complexes **63** synthesised with gaseous oxygen at -78°C leading to the dendritic complexes **64** have been measured (Scheme 5). The oxidation rate constant for the second-generation dendrimer **63**



Scheme 5





($R = G_2$), $k_2 = 1.3 \times 10^{-2}$ litre mol $^{-1}$ s $^{-1}$, appeared to be two orders of magnitude lower than that of the first-generation dendrimer ($R = G_1$), $k_2 = 1.39$ litre mol $^{-1}$ s $^{-1}$. The third-generation dendrimer ($R = G_3$) was resistant to oxidation under identical conditions.

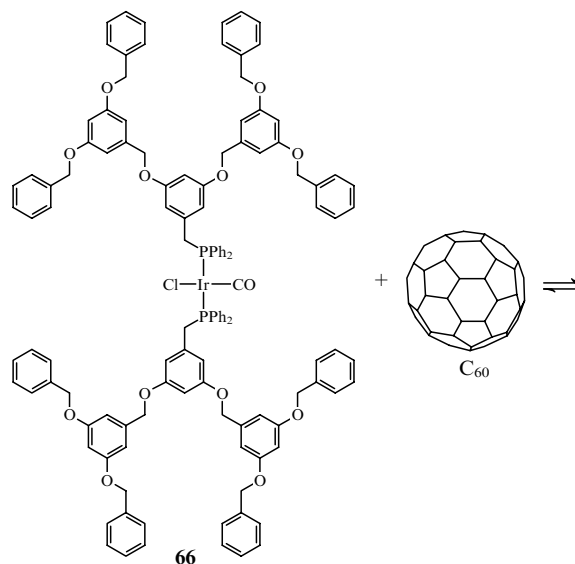
With an increase in temperature to -10 °C, the complexes **64** are decomposed as a result of intramolecular oxidation with the cleavage of the C–N bond. The half-life of the non-dendritic complex **64** ($R = G_0$) is 7 s, whereas those of the first- ($R = G_1$) and second-generation ($R = G_2$) dendrimers are 24 and 3075 s, respectively, which seems to be due to steric hindrances in the transition state of the decomposition reaction created by the dendritic substituents. This opens a way to the synthesis of thermally stable bimetallic complexes mimicking the effects of enzymes.

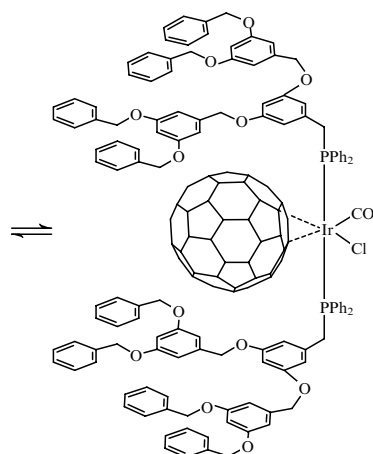
A method for encapsulation of noble metal microparticles in the core of polyamidoamine dendrimers (PAMAM) has been proposed.^{79–81} To obtain such materials, Pd(II) or Pt(II) cations were adsorbed by a polyamidoamine dendrimer containing hydroxy groups in the centre of the molecule with subsequent reduction with NaBH $_4$.⁷⁹ Such dendrimers contain microparticles of noble metals in their central fragment and are readily soluble in water, which makes it possible to conduct organic reactions (*e.g.*, hydrogenation of alkenes) involving these species in the aqueous phase.⁷⁹ The solubility of such catalysts in non-polar solvents can be increased through the use of surfactants, *e.g.*, fatty acids, which form salts with the surface amine groups of the dendrimer.⁸⁰ The use of perfluorinated carboxylic acids in biphasic systems containing perfluorinated solvents presents special interest, since this allows easy separation of the catalyst from the reaction product after the termination of the reaction.⁸¹

Metallodendrimers of the zero, first, second, third and fourth generations which contain Fe $_4$ S $_4$ (S $_4^{2-}$) as the dendrimer core and

can exist in two stable oxidation states, which can be used for storage of information, have been synthesised.⁸² The dendritic shell in compound **65** prevents possible electron transfer between closely arranged molecules, which would result in the loss of stored information.⁸² Voltammetric studies demonstrated that the electron transfer to the core of the molecule becomes more difficult with an increase in the number of the dendrimer generations.⁸²

The iridium complex with dendritic phosphine ligands **66** was used for reversible binding of fullerene C $_{60}$.⁸³ The complex **66** was





prepared by the reduction of Na_3IrCl_6 with carbon monoxide with subsequent attachment of dendritic phosphine ligands. On addition of fullerene to the bright yellow solution of the dendrimer **66**, the solution of the dendrimer–fullerene complex changes its colour to dark green.

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Chiral P,N-bidentate ligands in coordination chemistry and organic catalysis involving rhodium and palladium

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Abstract. Published data on the synthesis of rhodium and palladium complexes with optically active P,N-bidentate ligands and their applications in homogeneous asymmetric catalysis are summarised and discussed. The effect of the nature of the P,N-bidentate compounds on the structure of the metal complexes and on enantioselectivity in catalysis is examined. Allylic substitution, cross-coupling, hydroboration and hydrosilylation catalysed by Rh or Pd complexes with optically active P,N-bidentate ligands are considered. The prospects for the development of this field of chemistry are demonstrated. The bibliography includes 186 references.

I. Introduction

A fundamental problem studied at the border of chemical disciplines is the coordination behaviour of bi- and polyfunctional ligands. This problem includes competition of ligands for metal atoms, donor–acceptor interactions, isomerism of complexes, stereo- and regioselective synthesis of coordination compounds and specific complex formation in biologically important objects.¹ Of particular interest are phosphorus-containing compounds, which play an extremely important role in the development of views on coordination bonds, the geometry and the structure of complexes and on the mutual influence of inner-sphere ligands as well as in metal complex catalysis.^{2,3} Systems containing an electron-donating centre of a different nature, apart from the phosphorus centre, are being vigorously studied. P,N-Bidentate ligands are highly important. They simultaneously exhibit properties of both soft and hard bases and promote redistribution of functions in a catalytic cycle, formation of bimetallic structures and a specific arrangement of the metal coordination sphere. Thus P,N-bidentate ligands can provide *cis*- or *trans*-chelation, bridging binding in either the ‘head-to-tail’ or ‘head-to-head’ fashions (in particular, in structures with metal–metal bonds) and P-mono-dentate coordination. The particular type of coordination

depends, first of all, on the length of the bridge linking the donor atoms. Systems with two linking units are typical chelating agents; the bridging type of coordination is barely known for them, whereas three-unit species are capable of bridging coordination. Coordination of a P,N-system to a central atom gives rise to two moieties differing in kind, containing electron-donating centres with different steric and electronic characteristics. Being structurally asymmetric, P,N-bidentate ligands also possess clear-cut electronic asymmetry. In addition, both steric and electronic parameters of the electron-donating centres and the nature of the bridge linking them can be varied over wide limits. The features listed above are important in asymmetric catalysis in which very fine structural and electronic changes in the ligand nature can be significant. Therefore, it is quite natural that the greatest progress in the enantioselective catalysis of cross-coupling, allylation, hydroboration, hydrosilylation and other processes has been achieved by the use of metal complexes with P,N-bidentate chiral ligands.

Data on the role of optically active P,N-bidentate ligands in the coordination chemistry and catalysis are reported in several monographs and reviews.^{4–10} However, the information presented there concerns either a particular narrow group of compounds (for example, ferrocenyl systems⁸) or a particular catalytic reaction. The present review is the first attempt to summarise and describe systematically the role of chiral P,N-bidentate ligands in coordination chemistry and asymmetric catalysis. Attention is concentrated on the studies published over the last 15 years, most of all, in the 1990s, which were the years of vigorous development of the field of chemistry in question. This review deals only with P,N-bidentate systems with no additional electron-donating centres (*i.e.* devoid of O, S, Se and As or additional N or P atoms), only rhodium and palladium complexes being considered. Although examples of the use of W(0),¹¹ Au(I),^{12,13} Ir(I)¹⁴ and Pt(II)¹⁵ complexes in enantioselective catalysis do exist, the leading position of the two above-mentioned metals is beyond doubt.

We have classified the published data on the basis of the ligand structure. This approach appears expedient because it allows one to cover the achievements of both coordination chemistry and catalysis. Classification in terms of the types of organic reactions is more reasonable in considering the problems of enantioselective catalysis, whereas that accepted in coordination chemistry is based on the nature of the metal and the main initial metal complexes used. When these two aspects are discussed simultaneously, the nature of the P,N-bidentate ligand is a unifying point. Phosphorus-substituted ferrocenes and dihydrooxazoles are the subjects of separate Sections. This is due to the outstanding role of

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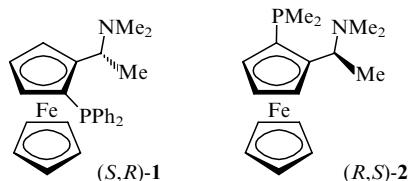
Uspekhi Khimii 69 (8) 721–743 (2000); translated by Z P Bobkova

these derivatives in asymmetric catalysis. Ligands of this type ensure high yields and high enantioselectivity of processes and provide the possibility of investigating some aspects of the catalysis mechanisms, for example, the role of the planar chirality of the ferrocenyl fragment. Phosphorus-substituted dihydrooxazoles represent a specific group of ligands developed for highly efficient allylation. The change in the steric and electronic parameters of the sp^2 -hybridised donor nitrogen atom incorporated in the five-membered ring influences the properties of the ligand and the catalytic activity of its metal complexes. The rather patchy group of other ligands is classified according to the nature of the electron-donating nitrogen centre; compounds with the phosphite donor centre are distinguished as a separate group. In addition, in arranging the information, we attempted, whenever possible, to group studies of the most productive scientific schools chronologically and to consider comprehensively the most important catalytic processes.

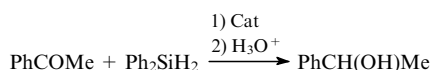
II. P,N-Bidentate phosphorus-substituted ferrocenes

1. Ligands with sp^3 -hybridised electron-donating nitrogen atoms. Aminoalkylferrocenylphosphines

In 1974, in the very beginning of the development of metal complex asymmetric catalysis, a publication appeared¹⁶ dealing with the synthesis of (S,R) -1-(1-dimethylaminoethyl)-2-diphenylphosphinoferrocene [(S,R)-**1**, (S,R)-PPFA][†] and (R,S) -1-(1-dimethylaminoethyl)-2-dimethylphosphinoferrocene [(R,S)-**2**, (R,S)-MPFA], which were the first representatives of chiral P,N-bidentate phosphorus-containing ligands.



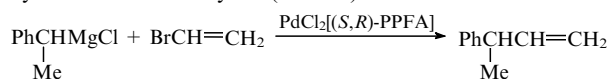
The novel ligands were tested¹⁶ in enantioselective hydro-silylation of a series of prochiral ketones. The best result (yield 89%, *ee* 49%) was obtained in the reaction of acetophenone with diphenylsilane in the presence of $[\text{Rh}(\text{C}_6\text{H}_{10}\text{Cl})_2]_2 \cdot 4\text{L}$, where $\text{L} = (R,S)$ -MPFA [(R,S)-**2**].



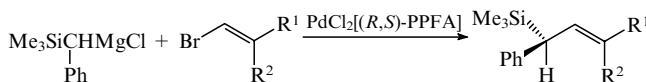
Cat = $[\text{Rh}(\text{C}_6\text{H}_{10}\text{Cl})_2]_2 \cdot 4(R,S)\text{-MPFA}$.

The compound (R,S) -**2** was found to be markedly more efficient than the best mono- and bidentate phosphorus-containing ligands known at that time, namely, (R) - $\text{PhCH}_2(\text{Ph})(\text{Me})\text{P}^*$ and 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [($-$)-DIOP].¹⁶ It was also found that replacement of the dimethylamino group in the side chain of the ligand (R,S) -**2** by a hydrogen atom results in a sharp decrease in the stereoselectivity. These studies opened up a new line in the search for bidentate chiral ligands for metal complex catalysis. The researchers used simultaneously two fruitful concepts, namely, combination of two different electron-donating centres (phosphorus and nitrogen) and two types of chirality (central and planar) in the molecule of an optically active ligand. PPFA [(S,R)-**1**] has been modified, for example, by replacing the methyl substituents at the nitrogen atom by Et, Pr^i , Bu^i , etc.¹⁷ P,N-Bidentate ligands have been assayed in other asymmetric catalytic processes. Cross-coupling of (1-phenylethyl)magnesium chloride with vinyl bro-

mide catalysed by the complex $\text{PdCl}_2[(S,R)\text{-PPFA}]$ gave (S) -3-phenylbut-1-ene in 82% yield (*ee* 61%).^{17,18}



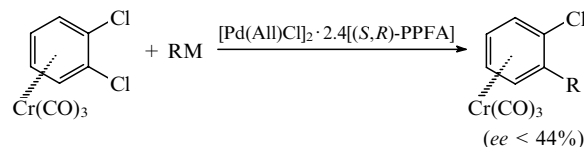
The enantiomer of the ligand (S,R) -**1**, namely, (R,S) -PPFA, also as a complex with PdCl_2 , ensures an even higher enantioselectivity in this type of reaction.¹⁹



$\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{H}$ (*ee* 85%); $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$ (*ee* 95%);

$\text{R}^1 = \text{R}^2 = \text{H}$ (*ee* 96%).

The bidentate ligand (S,R) -**1** is able to induce not only central but also planar chirality.²⁰

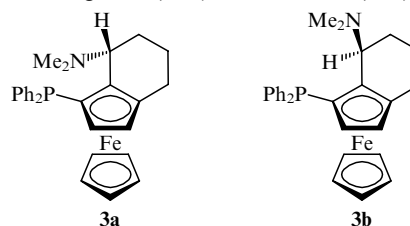


$\text{R} = \text{CH=CH}_2$, C(Me)=CH_2 , CH=CHBu ;

$\text{M} = \text{SnBu}_3$, MgCl , ZnCl , B(OH)_2 ; $\text{All} = \text{CH}_2=\text{CHCH}_2$.

For (S,R) -**1** and for its close analogue having two *tert*-butyl substituents at the phosphorus atom, a number of rhodium(I) cationic complexes, including $[(\text{NBD})\text{Rh}(\text{L})]^+\text{X}^-$ (NBD is norbornadiene, $\text{X}^- = \text{PF}_6^-$, ClO_4^-), $[(\text{COD})\text{Rh}(\text{L})]^+\text{Y}^-$ (COD is cyclooctadiene, $\text{Y}^- = \text{BF}_4^-$, BPh_4^-), have been prepared. The complexes have been thoroughly studied by ^1H NMR, ^{31}P NMR and IR spectroscopy and conductivity. The structure of the complex $\{(\text{NBD})\text{Rh}[(R,S)\text{-PPFA}]\}^+\text{PF}_6^-$ was established by X-ray diffraction analysis.²¹ The formation of a metal-containing chelate ring was demonstrated in all cases. The use of these complexes as catalysts of hydrogenation of *N*-acetyl- α -aminocinnamic acid ensures *ee* of up to 84%.^{21,22}

The further investigation into chiral phosphorus-containing ferrocenes has been mostly carried out by two research groups, namely, Weissensteiner's^{23–28} and Togni's^{29–39} groups. Thus Weissensteiner *et al.*^{23,24} synthesised epimeric ferrocenyl P,N-bidentate ligands, (R,R) -PTFA **3a** and (R,S) -PTFA **3b**.

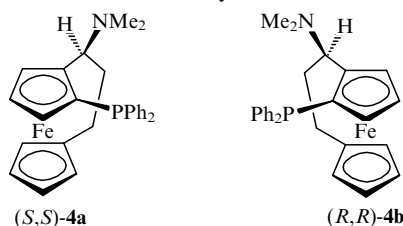


In the model cross-coupling of (1-phenylethyl)magnesium chloride with vinyl bromide, the complex $\text{PdCl}_2[(R,R)\text{-PTFA}]$ provides an *ee* of 79% for a nearly quantitative chemical yield of 3-phenylbutene; in the presence of $\text{PdCl}_2[(R,S)\text{-PTFA}]$, the *ee* is only 4%. Thus, in this case, the process enantioselectivity is governed by the central chirality of the ligands **3a,b**. This outcome contrasts sharply with the results obtained in the catalysis by nickel complexes, which gave close values of the optical yield in the presence of (R,S) - and (R,R) -PPFA.¹⁷ The structure of the catalyst $\text{PdCl}_2[(R,R)\text{-PTFA}]$ was studied by ^1H , ^{13}C and ^{31}P NMR spectroscopy. According to X-ray diffraction data, the $\text{Pd}-\text{P}$ bond length [2.207(2) Å] is close to the average values observed in *cis*-palladium(II) dichloride complexes with aminophosphine ligands.²⁴ Subsequently, the palladium(II) complex $\{\text{Pd}(\eta^3\text{-C}_4\text{H}_7)[(R,R)\text{-PTFA}]\}^+\text{Tf}^-$ and the palladium(0) complex $\{\text{Pd}[(R,R)\text{-PTFA}]\}_2\text{L}$, where $\text{Tf} = \text{CF}_3\text{SO}_3$, L is maleic anhydride or dimethyl fumarate, have been studied in detail²⁵ using multi-nuclear NMR data (including the INDOR and EXSY techniques)

[†] Hereinafter, the first character denotes the configuration of the ferrocenyl core.

and X-ray diffraction analysis. It was concluded that PTFA, which is conformationally more rigid than PPFA, possesses also stronger chelating properties. An attempt²⁶ to use (*S,S*)-PTFA as a ligand in asymmetric hydroformylation of styrene proved unsuccessful: for rhodium(I)-based catalyst, *ee* was 0.5%, while in the case of platinum(II)-based catalyst, it is 7%–21%. This was explained²⁶ by the fact that the chelate angle formed by PTFA is rather small, especially in the case of complexation with platinum(II).

Enantiomeric ferrocenyl bidentate ligands **4a,b**, related in structure to PPFA and PTFA, have been prepared.^{27,28} Complexes of the ligand **4a** with PdCl₂ and the ligand **4b** with PdClMe, PdMe₂ and PdPh₂ were synthesised.

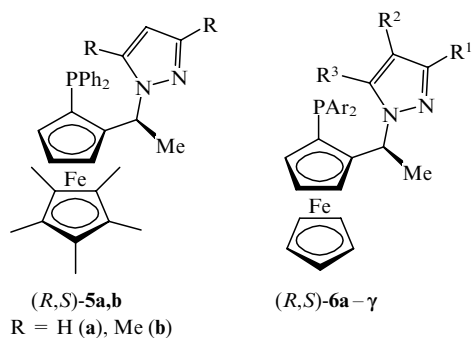


The structures of the ligands **4a,b** and complexes derived from them, which are promising in asymmetric catalysis, were studied by X-ray diffraction analysis and multinuclear NMR spectroscopy including low-temperature procedures. Broadening of the resonance signals of the diastereotopic methyl groups in the palladium complexes of **4a,b** suggests²⁸ that the energy barrier to the rupture of the Pd–N bond is low.

2. Ligands with *sp*²-hybridised electron-donating nitrogen atoms

a. Ferrocenylphosphinopyrazoles

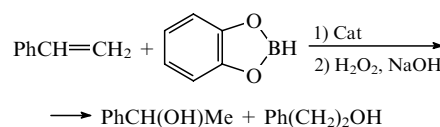
Researches into ferrocene-based P,N-bidentate ligands have gained a new incentive due to the studies of Togni *et al.*^{29–39} Having started with minor structural changes, *i.e.* introduction of one or five methyl groups into the unsubstituted ring of (*S,R*)- or (*R,S*)-PPFA,²⁹ they used subsequently a fairly advantageous expedient, namely, they replaced the dimethylamino group by a pyrazole ring. This gave rise to a series of 1-diarylphosphino-2-[1-(pyrazol-1-yl)ethyl]ferrocenes **5a,b**²⁹ and **6a–g**.^{30–32}



Compound 6	R ¹	R ²	R ³	Ar
a	H	H	H	Ph
b	Me	H	Me	Ph
c	CF ₃	H	CF ₃	Ph
d	Me	Me	Me	Ph
e	CF ₃	H	Me	Ph
f	Pr ⁱ	H	Pr ⁱ	Ph
g	Me	Br	Me	Ph
h	Ph	H	Me	Ph
i	Me	NO ₂	Me	Ph
j	Ph	H	Me	cyclo-C ₆ H ₁₁
k	Me	H	Me	4-FC ₆ H ₄
l	Me	H	Me	4-CF ₃ C ₆ H ₄
m	Me	H	Me	4-MeOC ₆ H ₄

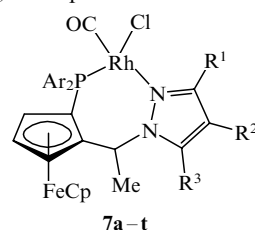
Compound 6	R ¹	R ²	R ³	Ar
n	Me	H	Me	3,5-Me ₂ C ₆ H ₃
o	Me	H	Me	4-MeC ₆ H ₄
p	Me	H	Me	4-PhC ₆ H ₄
q	Me	H	Me	3,5-(CF ₃) ₂ C ₆ H ₃
r	Me	H	Me	4-NMe ₂ C ₆ H ₄
s	CF ₃	H	CF ₃	4-MeOC ₆ H ₄
t	1-naphthyl	H	Me	Ph
u	1-adamantyl	H	H	Ph
v	cyclo-C ₆ H ₁₁	H	Me	Ph
w	Ph	H	H	Ph
x	2-naphthyl	H	Me	Ph
y	4-pyridyl	H	Me	Ph
z	3-NO ₂ C ₆ H ₄	H	H	Ph
α	2,4-(MeO) ₂ C ₆ H ₃	H	Me	Ph
β	9-anthryl	H	Me	Ph
γ	9-triptycyl	H	H	Ph

The ligands **6a–t** were tested^{30,31} in the hydroboration–oxidation of styrene with catecholborane.



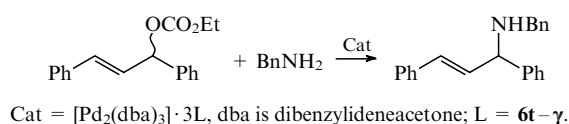
Cat = {[Rh(COD)₂]⁺BF₄[−]} (–**6a–t**).

In some cases, the reaction gives a substantial amount of an achiral primary alcohol but, in general, the enantioselectivity is high. The optical yield was found to be clearly dependent on the electronic properties of substituents at the donor centres — electron-withdrawing substituents in the pyrazole nucleus decrease the optical yield, whereas substituents in the phenyl groups at the phosphorus atom increase the optical yield [the *ee* values for the formation of (*R*)-1-phenylethanol in the presence of the ligands **6c, e, a, l, q** are 33%, 44%, 65%, 98% and 98.5%, respectively]. Rhodium(I) chloro carbonyl complexes **7a–t** were synthesised by reactions of **6a–t** with [Rh(CO)₂Cl]₂. They were characterised by the data of ¹H, ³¹P (¹J_{P–Rh} = 161–176 Hz) and ¹³C NMR and IR spectroscopy (*ν*_{CO} = 1980–2008 cm^{−1}) and mass spectrometry.³¹ X-ray diffraction analysis of the compounds **7n, o** was performed.³¹



An acceptable correlation has been found between the *ν*_{CO} and *ee* values for the complexes **7a–t**; the frequency of the carbonyl group vibrations is affected by changes in the σ-donor properties of the nitrogen centre and in the π-acceptor properties of the phosphorus centre. The cationic complexes [Rh(COD)(L)]⁺BF₄[−] have been prepared (L = **6b, c**) and also studied by multinuclear magnetic resonance and X-ray diffraction analysis. As in the complexes **7a–t**, in this case, too, a seven-membered chelate metallacycle is formed.

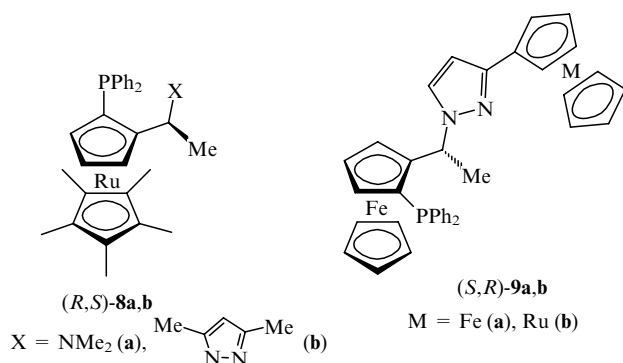
The ligands **6t–γ** have found application in a reaction significant from the synthetic standpoint, namely, allylic amination³² (the enantioselectivity reaches 99%).



The reaction mechanism, including allylic intermediates $[\text{Pd}(\eta^3\text{-PhC}_3\text{H}_3\text{Ph})(\text{L})]^+\text{PF}_6^-$, was studied in detail using X-ray diffraction analysis and 2D NMR. It was found that the attack of a nitrogen-containing nucleophile is directed at the carbon atom in the allylic ligand located in the *trans*-position relative to the phosphorus centre of the coordinated P,N-bidentate ligand. The activation barrier to the formation of the C–N bond in the *trans*-position relative to the phosphorus atom is 3 kcal mol⁻¹ lower than that for the *trans*-position to nitrogen.³² Calculation methods³³ and conformational analysis³⁴ [using ³¹P, ¹³C and ¹H (NOESY) data] of model allylic complexes have also been invoked to study the reaction mechanism and stereochemical features of the process.

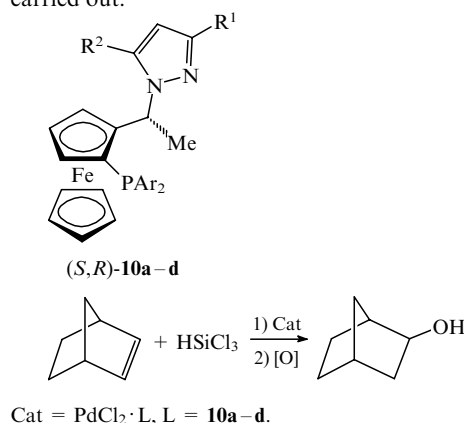
The ligand **6u**, containing an adamantyl substituent in the pyrazole ring, proved to be the most efficient in allylic amination (*ee* 99%).^{32,35} By the addition of coordinating anions, F⁻, BH₄⁻ or OH⁻, in co-catalytic amounts, a virtually quantitative optical yield can be attained (>99.5%).³⁶

Similar derivatives of ruthenocene **8a,b**³⁷ and bimetallic systems **9a,b**, in which the pyrazole ring contains a second ferrocene fragment, have been synthesised.³⁸



The efficiencies of the ligands **6u** and **9a,b** in the catalysed allylic amination are comparable (*ee* >99.5%).³⁸ In catalytic hydroboration–oxidation, the ligand **8b** is somewhat inferior to the ferrocenyl analogue **5b** (the optical yields for 100% conversion of styrene are 87% and 94%, respectively).³⁷

Recently,³⁹ ligands **10a–d**, close analogues of the compounds **6a–γ**, have been proposed. In the presence of these ligands, asymmetric hydrosilylation–oxidation of norbornene has been carried out.

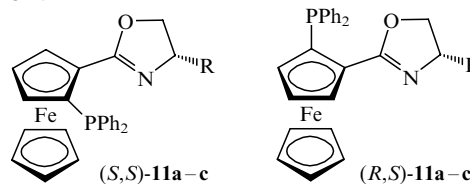


Compound 10	R ¹	R ²	Ar	Optical yield of hydroxy-norbornane (%)
a	Ph	Me	Ph	39
b	2,4,6-(MeO) ₃ C ₆ H ₂	H	Ph	82
c	2,4,6-Me ₃ C ₆ H ₂	H	Ph	91
d	2,4,6-Me ₃ C ₆ H ₂	H	3,5-(CF ₃) ₂ C ₆ H ₃	99

In the case of the ligands **10**, the optical yield increases on passing from **10a** to **10d**. It has been concluded³⁹ that optimisation of the ligand regarding steric factors should be done with allowance for its electronic asymmetry because the σ-basicity of the pyrazole fragment and the π-acidity of the phosphine fragment are important in hydroxylation–oxidation, as well as in hydroboration–oxidation.

b. Phosphinoferrocenyl-4,5-dihydrooxazoles

Phosphinodihydrooxazole ligands will be discussed in Section III. This Section is devoted to structures related to the ligands **6a–γ** but having a second chiral centre in the heterocyclic fragment. In particular, epimeric ligands of type **11a–c** have been synthesised.^{40–43} They are designated by the common abbreviation DPOF.



R = Prⁱ (a), Bu^t (b), Me (c).

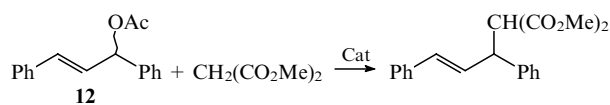
The reaction of the compounds (S,S)- and (R,S)-**11b** with PdCl₂(MeCN)₂ gave complexes {PdCl₂[(S,S)-**11b**]} and {PdCl₂[(R,S)-**11b**]}; the latter was characterised by X-ray diffraction analysis.⁴⁰ These complexes were used as cross-coupling catalysts.



R = H, Ph; Cat = [Pd(All)Cl]₂L, L = (S,S)-**11a**, (S,S)-**11c**, (S,R)-**11a**.

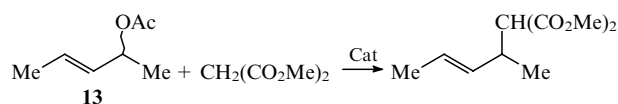
The complex {PdCl₂[(S,S)-**11a**]} provides a higher enantioselectivity of this process than its epimer (*ee* 45% and 8%, respectively). The chemical yield is also substantially greater in the former case (74% and 23%, respectively). Thus, unlike the ligands (R,R)-PTFA **3a** or (R,S)-PTFA **3b**, in this case, the enantioselectivity is mainly due to planar chirality.

In the classical alkylation of malonates with allyl esters catalysed by [Pd(All)Cl]₂, the ligand (S,S)-**11b** ensures *ee* 90%; in the case of the ligand (S,S)-**11c**, the enantioselectivity is more than 99% (the chemical yield is nearly quantitative in both cases). In the presence of (R,S)-**11b**, *ee* is only 73%.^{42,43} In this reaction, the crucial role is also played by the stereochemistry of the ferrocenyl core of the ligand.



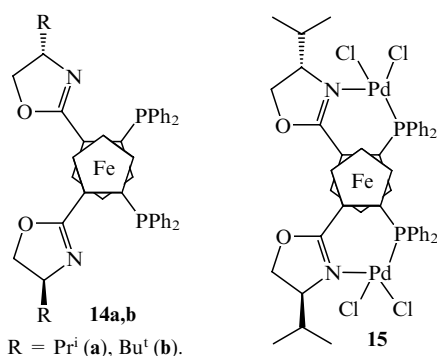
Cat = [Pd(All)Cl]₂L, L = (S,S)-**11b**, (S,S)-**11c**, (R,S)-**11b**.

The enantioselectivity of the reaction depends also on the steric requirements of the substrate. On passing from 1,3-diphenylprop-2-enyl acetate **12** to the methyl analogue **13**, the optical yield sharply drops (it is not more than 36%).



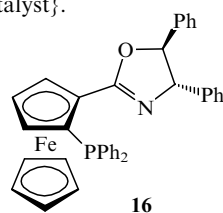
Cat = [Pd(All)Cl]₂L, L = (S,S)-**11b**.

Tetrasubstituted ferrocenyl ligands **14a,b**, constructed as combinations of two fragments of the ligands **11a** or **11b**, have also been synthesised.⁴⁴



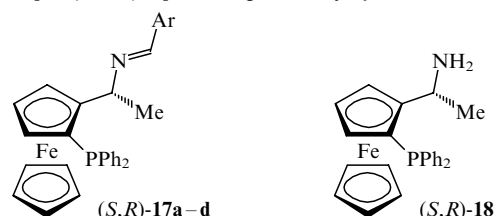
The compound **14a** was converted into the palladium complex **15**; unfortunately, this complex was only scantily characterised by spectroscopic data (data on ¹H NMR and mass spectra were reported). Interestingly, the ligand prepared by replacement of the dihydrooxazole rings in the structure **14a** by the CH(Me)NMe₂ groups behaves as a P,P- rather than a P,N-bidentate ligand with respect to Pd(II) because the amino-group nitrogen atom is bound to palladium more weakly than the dihydrooxazole nitrogen.⁴⁴ In the Pd(II)-catalysed alkylation of the allyl acetate **12**, the ligands **14a,b** provide *ee* 96%–99%, the chemical yield being more than 90%; the epimer of compound **14a** with the opposite planar configuration displays the same enantioselectivity. Thus, in this case, unlike the ligands **11**, the planar chirality does not have a governing influence on the product configuration; this might be due to different reaction mechanisms.

Ligand (*S,S,S*)-DIPOF **16** has been studied^{14,45} in the asymmetric reduction of a series of prochiral aromatic and aliphatic ketones with diphenylsilane {with [Rh(COD)Cl]₂ as the pre-catalyst}.



The chemical yields in these reactions were 45%–100%, while the optical yields were 57%–91%. The best results were attained in the reduction of acetophenone to (*R*)-1-phenylethanol. In the presence of (*R,R,R*)-DIPOF, the reaction affords (*S*)-1-phenylethanol with *ee* 91%. The use of [Ir(COD)Cl]₂ as the pre-catalyst increases the optical yield to 96%.

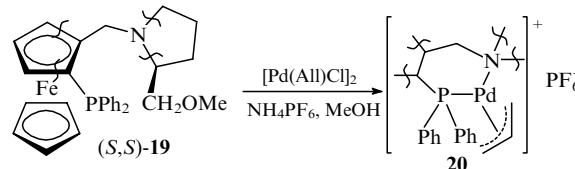
In the hydrosilylation of acetophenone with diphenylsilane, the use of related dihydrooxazole systems, namely, arylideneaminoalkylferrocenylphosphines **17a–d** leads to commensurable results (*ee* 87%–90% for chemical yields of 86%–94%)⁴⁶ {with [Rh(NBD)Cl]₂ as the pre-catalyst}.



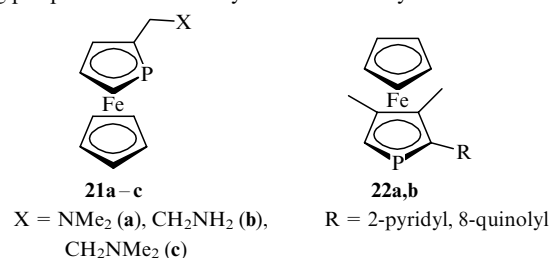
Ar = Ph (**a**), 3-CF₃C₆H₄ (**b**),
4-CF₃C₆H₄ (**c**), C₆F₅ (**d**)

The presence of the imino group in the ligand structure is of prime importance. Indeed, in the presence of the amine (*S,R*)-**18**, *ee* is 39%, while in the presence of (*S,R*)-PPFA [(*S,R*)-**1**], it is only 16%. However, the nature of the arylidene group barely influences the optical yield.

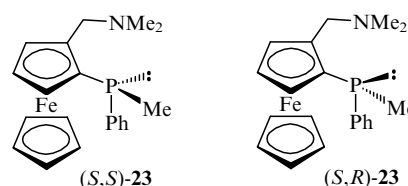
In conclusion, we would like to mention several other P,N-bidentate phosphorus-substituted ferrocenes which hold prospects as asymmetric catalysts. The first one is ligand **19**, for which cationic complex **20** has been obtained.⁴⁷ The P,N-bidentate manner of binding to palladium(II) in the complex **20** was established by ¹H, ³¹P and ¹³C NMR spectroscopy and X-ray diffraction analysis.



Phosphaferrocenes **21a–c**, representing a new class of ligands with planar chirality,⁴⁸ and analogous compounds **22**,⁴⁹ containing peripheral aza heterocycles have been synthesised.



A recent publication⁵⁰ describes the synthesis and resolution of diastereomers (*S,S*)-**23** and (*S,R*)-**23** with a chiral centre on the phosphorus atom.



A complex of the compound (*S,R*)-**23** with PdI₂ — [(1-MePhP-2-Me₂HN⁺CH₂C₅H₃)FeC₅H₅][PdI₃[−]] — has been prepared.⁵⁰ X-Ray diffraction analysis showed a P-monodentate binding to palladium of the ligand protonated at the nitrogen atom. The researchers suggested that the complex was formed upon opening of the chelate ring on treatment with the hydrogen iodide, resulting from decomposition of PdI₂, followed by the reaction of I₂ with traces of water. Hence, it was concluded that the six-membered metallacycle involving the ligand (*S,R*)-**23** is relatively unstable. However, this statement seems arguable because lots of metal complexes formed by related systems, for example, PPFA **1**, PTFA **3** or the ligands **4a,b** are known. The wrong choice of the initial palladium(II) compound appears to be a more probable reason.

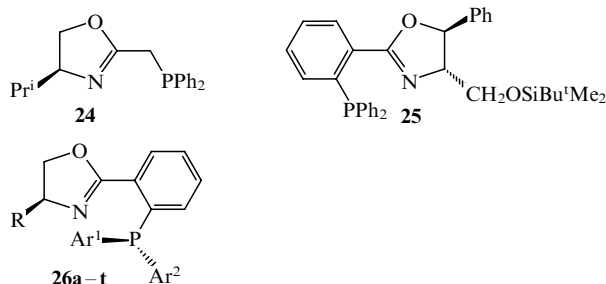
Thus, the use of nitrogen-and-phosphorus-containing ferrocenes in asymmetric metal complex catalysis makes it possible to attain more than 90% optical yields in some important reactions such as cross-coupling, hydroboration–oxidation and hydrosilylation–oxidation of alkenes, hydrosilylation of ketones, and allylic substitution.

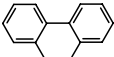
III. P,N-Bidentate phosphorus-containing 4,5-dihydrooxazoles

This group of ligands includes compounds containing an *sp*²-hybridised donor nitrogen atom.

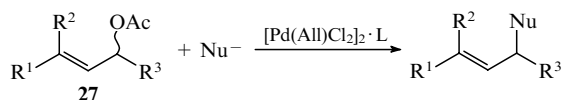
In 1993, three research groups working independently, namely, Helmchen's group⁵¹ from the Institute of Organic Chemistry of Heidelberg University, Williams' group⁵² from the Technological University (Lawboro), and Pfaltz's⁵³ group from the Institute of Organic Chemistry of Basel University, reported almost simultaneously the synthesis and the use in enantiomeric catalysis of the first representatives of a new class of P,N-bidentate

ligands — phosphorus-containing 4,5-dihydrooxazoles. There is an opinion,⁵⁴ however, that Williams *et al.*⁵⁵ came out with the main concepts a year earlier. Subsequently, the effort of the three groups mentioned above resulted in the synthesis of a large series of phosphorus-substituted dihydrooxazoles such as **24**, **25** and **26a–t**.^{56–76}



Compound 26	Ar ¹	Ar ²	R
a	Ph	Ph	Me
b	Ph	Ph	Pr ⁱ
c	Ph	Ph	Bu ^t
d	Ph	Ph	Bu ⁱ
e	Ph	Ph	Ph
f	Ph	Ph	CH ₂ Ph
g	Ph	Ph	1-naphthyl
h	Ph	Ph	CH ₂ Bu ^t
i	Ph	Ph	CH ₂ SBu ⁱ
j	Ph	Ph	CMe ₂ SCH ₂ Pr ⁱ
k	Ph	Ph	(CH ₂) ₂ SMe
l	Ph	Ph	(3-indolyl)methyl
m	Ph	1-naphthyl	Pr ⁱ
n	1-naphthyl	Ph	Pr ⁱ
o	1-naphthyl	1-naphthyl	Pr ⁱ
p	2-biphenyl	Ph	Pr ⁱ
q	2-biphenyl	Ph	Ph
r	3,5-(CF ₃) ₂ C ₆ H ₃	3,5-(CF ₃) ₂ C ₆ H ₃	Pr ⁱ
s	cyclo-C ₆ H ₁₁	cyclo-C ₆ H ₁₁	Pr ⁱ
t		Pr ⁱ	

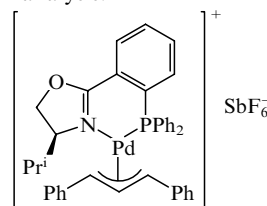
When ligands of the type **26** are employed in the model alkylation of dimethyl malonate with the allyl acetate **12** [with [Pd(All)Cl]₂ as the pre-catalyst],^{51–53,56} optical and chemical yields reach 99%. The highest enantioselectivity is exhibited by the chiral substituted dihydrooxazoles **26b, c, e**. Other nucleophilic substitution reactions at the allylic carbon atom in the allyl acetates **27** were also performed with high enantioselectivity in the presence of these compounds. The results are summarised in Table 1.



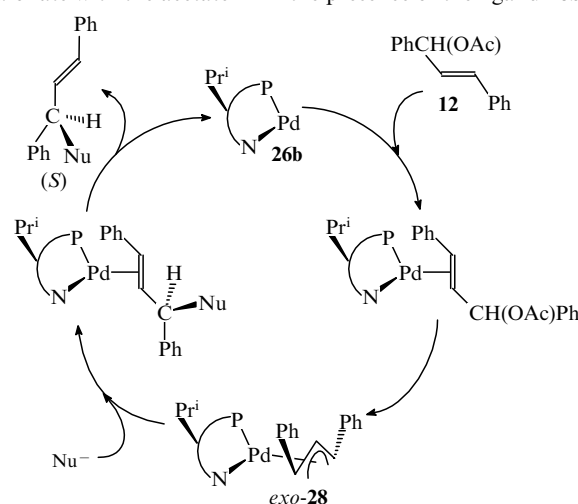
It should be noted that, in the presence of the epimeric compounds **26m, n**, the corresponding derivatives are formed in the same optical yield (77%) and with the same (*S*) absolute configuration, *i.e.* the asymmetric induction is accomplished by the dihydrooxazole fragment.⁵⁶ The distance between the electron-donating centres is also significant — the ligand **24**, which forms a five-membered metal-containing chelate ring, provides a moderate selectivity (*ee* 73%).⁵¹

Several palladium-catalysed intramolecular alkylation reactions have also been successfully performed;⁶⁷ the best result was attained with the ligand **26e** (*ee* 80%–87%). Enantioselective allylic substitution is utilised to prepare natural products including optically active starting compounds for the synthesis of α - and

β -amino acids and their derivatives.^{58,66} A palladium(II) cationic complex was prepared from the compound **26b** and characterised by ¹H NMR spectroscopy (NOESY, ROESY) and X-ray diffraction analysis.



Resorting to low-temperature 2D NMR spectroscopy made it possible to propose a catalytic cycle for the alkylation of dimethyl malonate with the acetate **12** in the presence of the ligand **26b**.⁶⁸

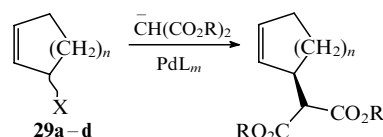


Nu = CH(CO₂Me)₂.

The predominant (*S*)-enantiomer of the reaction product is formed *via* an attack by the nucleophile on the C(3) atom of the allylic fragment, located in the *trans*-position relative to the phosphorus centre, in the *exo*-**28**.

Detailed investigation of the reaction mechanism using model reactions permitted ligands of the type **26** to be employed in other asymmetric allylic substitution processes. Thus *ee* values of more than 99.9% are attained in some cases in the alkylation of nitromethane with the allyl carbonates RCH=CHCH(R)O.CO₂Me (R = Me, Et, Ph).⁶⁹ Among the ligands **26b, c, e, i, m, n, o** tested [with [Pd₂(dba)₃]·CHCl₃ as the pre-catalyst], the best results were obtained for **26b, c, i**.

In the case of cyclic substrates **29**, the best results were obtained for the ligands **26p, q**.⁷⁰ The epimeric compounds **26m, n** provide close enantioselectivities.

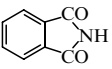


$n = 1$ (**a**), 2 (**b**), 3 (**c**), 4 (**d**); X = OAc, OCO₂Me, Br; R = Me, Et;
 $m = 1.5–3$; L = **26b, m, n, p, q**.

Phosphorus-containing cymantrenyldihydrooxazoles **30a–i** and **31a, b**⁷¹ ensure better asymmetric induction in some cases [with [Pd(All)Cl]₂ as the pre-catalysts].

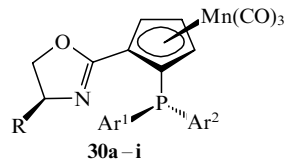
In the reaction of the cyclic allyl acetates **29a, b, c** (X = OAc) with the anion derived from dimethyl malonate in the presence of the ligand **30d**, the optical yields are 96%, 93% and >99%, respectively. The configuration of the phosphorus centre is of fundamental importance in this case: in the presence of the epimeric ligand **30c**, the reaction with the compound **29b** results in *ee* of only 31%. Compounds achiral at phosphorus (including

Table 1. Enantioselectivity in allylic substitution in the compounds **27** in the presence of the ligands **26b,c,e**.

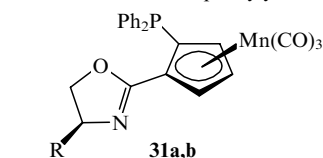
Compound 27	R ¹	R ²	R ³	HNu	L	Yield (%)	ee (%)	Ref.
a	Ph	H	Ph	CH ₂ (SO ₂ Ph) ₂	26b	78	93	57
				H ₂ NSO ₂ C ₆ H ₄ -4	26b	84	90	58
					26b	65	96	58
				(Ph) ₂ C=NCH ₂ P(O)(OEt) ₂	26b	98	96	59
				(Ph) ₂ C=NCH ₂ CO ₂ Bu ^t	26c	89	97	60
				CH ₂ (CO ₂ Me) ₂	26e	98	97	53
				H ₂ NNHBz	26c	95	97	61
				CH(NHAc)(CO ₂ Et) ₂	26e	98	97	53
				HO ₂ SBu ^t	26b	69	91	62 ^a
				HO ₂ SBu ^t	26c	70	90	62
				HO ₂ SBu ^t	26e	71	93	62
b	Et	H	Ph	CH ₂ (CO ₂ Me) ₂	26c	98	79	63
c	Me	H	Ph	CH ₂ (CO ₂ Me) ₂	26c	96	71	57, 63
				H ₂ NBn	26c	87	89	61
d	Pr ⁱ	H	P(O)(OEt) ₂ (see ^b)	HN(Boc) ₂ ^c	26c	29	97	61
e	Ph	Ph	Me	CH ₂ (CO ₂ Me) ₂	26b			64–66
f	Ph	Ph	Ph	CH ₂ (CO ₂ Me) ₂	26b			64–66
g	Ph	Ph		CH ₂ (CO ₂ Me) ₂	26b			64–66
				CH ₂ (CO ₂ Me) ₂	26c	88	96	53
h	Ph	Ph	Mes	CH ₂ (CO ₂ Me) ₂	26b			64–66
i	Pr ⁱ	H	Ph	CH ₂ (CO ₂ Me) ₂	26c			53

^a Pre-catalyst is [Pd₂(dba)₃] · CHCl₃; ^b the corresponding phosphate was used; ^c Boc is Bu^tOCO.

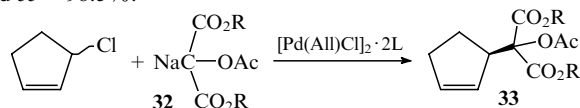
30a,b) are relatively ineffective, the *ee* values being not more than 44%.⁷¹



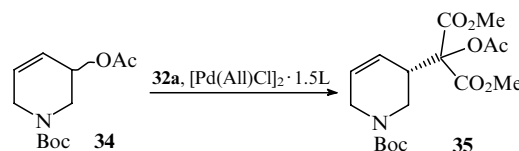
Compound 30	Ar ¹	Ar ²	R
a	Ph	Ph	Pr ⁱ
b	Ph	Ph	Bu ^t
c	Ph	2-biphenyl	Bu ^t
d	2-biphenyl	Ph	Bu ^t
e	3,5-Me ₂ C ₆ H ₃	2-biphenyl	Bu ^t
f	2-biphenyl	3,5-Me ₂ C ₆ H ₃	Bu ^t
g	3,5-(CF ₃) ₂ C ₆ H ₃	2-biphenyl	Bu ^t
h	2-biphenyl	3,5-(CF ₃) ₂ C ₆ H ₃	Bu ^t
i	2-biphenyl	2-biphenyl	Bu ^t

R = Prⁱ (**a**), Bu^t (**b**)

The ligand **30d** was also found to be highly effective in related reactions. Thus, when 3-chlorocyclopentene reacts with the sodium salt **32**, the reaction product **33** is formed in >94% yield and *ee* >98.5%.⁷²

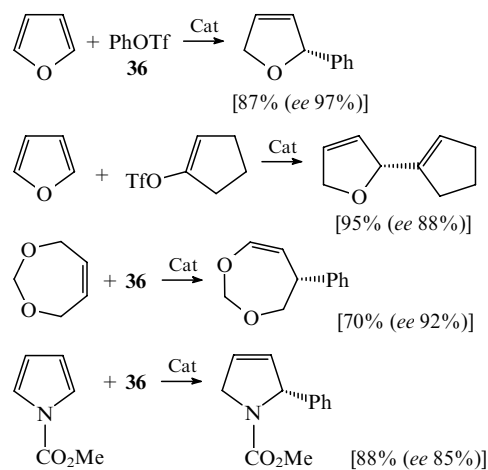
R = Me (**a**), Et (**b**); L = **30d**.

A similar reaction with the *N*-substituted tetrahydropyridine acetate **34** results in a product yield of 84% and *ee* 98%.⁷³

L = **30d**.

Compound **35** is a valuable optically active initial compound for the preparation of aza sugars and (*R*)-nicotinic acid.

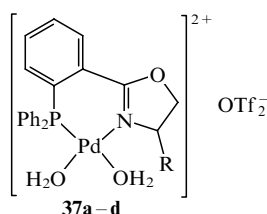
The use of phosphorus-containing dihydrooxazoles in the formation of the C–C bond according to the Heck reaction is equally effective. Thus the ligand **26c** ensures a fairly good enantioselectivity in the reactions with triflates.^{58, 74, 75}

Cat = [Pd(dba)₂] · 2L, L = **26c**.

In this reaction, phosphorus-substituted dihydrooxazoles are preferred over diphosphines including the known BINAP ligand [2,2'-bis(diphenylphosphino)-1,1'-dinaphthalene] because they do not induce undesirable side processes of double bond migration.⁷⁵

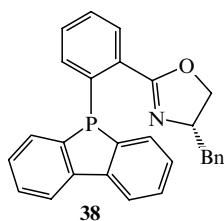
Complexes **37a–d**, prepared from the corresponding ligands and $\text{PdCl}_2(\text{MeCN})_2$ [followed by treatment with $\text{Ag}(\text{OTf})$ and water], have been employed for copolymerisation of styrene with CO.⁷⁶ This yielded poly(1-oxo-2-phenylpropane-1,3-diyl) with a molecular mass of $\sim 20\,000$.

In the presence of the achiral complex **37a**, an atactic polymer is formed, whereas catalysis by the optically active complexes **37b–d** results in a stereoregular isotactic polymer.



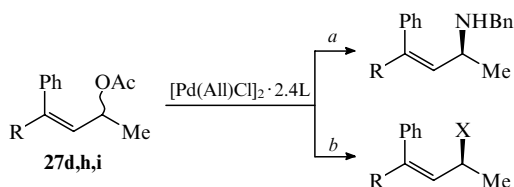
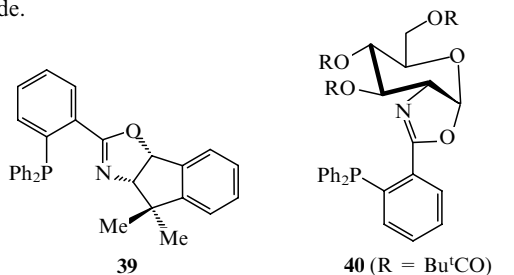
R = H (**a**), Bu^i (**b**), Ph (**c**), Bn (**d**).

Ligand **38** has been employed for copolymerisation of styrene and ethylene with CO in the presence of the complex $[\text{Pd}(\text{OAc})\text{LS}]^+ \text{TfO}^-$, where L = **38** and S is a solvent.⁷⁷



Other researchers working independently of the three leading groups mentioned above used successfully the ligands **26b,e** in allylic sulfonation,⁷⁸ while the ligand **26c** was used in the intramolecular Heck reaction.⁷⁹ The allylation mechanism was analysed theoretically by the extended Hückel method.⁸⁰

New phosphorus-containing oxazolines **39** and **40** have been synthesised. The ligand **39**⁸¹ ensures *ee* of 95%–99% in the allylic amination of the acetates **27d,h,i** with benzylamine or phthalimide.

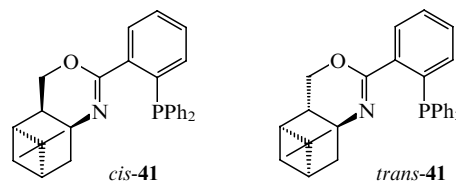


R = Ph (**d**, 43%, *ee* 99%), 4- ClC_6H_4 (**h**), 4- BrC_6H_4 (**i**); L = **39**;

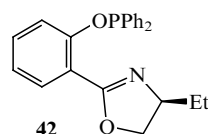
(a) BnNH_2 ; (b) HX, X =

The compound **40**, containing a carbohydrate fragment fused with a dihydrooxazole fragment, has been used as a ligand in the alkylation of dimethyl malonate with the allyl acetates **12** (*ee* 98%) and **13** (*ee* 69%) in the presence of $[\text{Pd}(\text{All})\text{Cl}]_2$.⁸² This resulted in the synthesis of phosphorus-containing dihydro-1,3-oxazine iso-

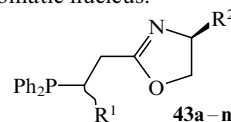
mers **41**. In the reaction with the allyl acetate **12** $\{[\text{Pd}(\text{All})\text{Cl}]_2$ as the pre-catalyst $\}$, *ee* depends on the ligand: it is 95% in the presence of *cis*-**41** and only 64% in the presence of *trans*-**41**.⁸³



On the basis of the compound **42**, neutral and cationic palladium(II) complexes have been prepared.⁸⁴ To the best of our knowledge, **42** is the only P,N-bidentate ligand of the dihydrooxazole type containing a phosphinite group. It would be of interest to study this compound in the asymmetric catalysis and to compare it with analogous phosphine systems.



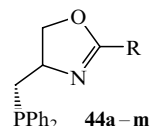
Recently, a series of phosphorus-containing dihydrooxazoles **43a–n** have been synthesised. Unlike the ligands **26–42**, in this case, the diphenylphosphine fragment is not attached to the aromatic nucleus.^{85,86}



$\text{R}^1 = \text{H}$; $\text{R}^2 = \text{Me}$ (**a**), Bn (**b**), Pr^i (**c**), Ph (**d**); $\text{R}^1 = (S)\text{-Me}$, $\text{R}^2 = \text{Pr}^i$ (**e**); $\text{R}^1 = (R)\text{-Me}$, $\text{R}^2 = \text{Pr}^i$ (**f**); $\text{R}^1 = (S)\text{-Ph}$; $\text{R}^2 = \text{Bn}$ (**g**), Pr^i (**h**), Ph (**i**), Bu^i (**j**); $\text{R}^1 = (R)\text{-Ph}$; $\text{R}^2 = \text{Bn}$ (**k**), Pr^i (**l**), Ph (**m**), Bu^i (**n**).

The alkylation with the allyl acetate **12** $\{[\text{Pd}(\text{All})\text{Cl}]_2$ as the pre-catalyst $\}$ in the presence of the ligands **43a–d** provides *ee* of 11%–90%, while this reaction in the presence of **43e–n** results in *ee* of 22%–98%. The best results were attained in the presence of the ligands **43c** and **43n**. The optical yield depends on the solvent; for example, with the ligand **43c** in CH_2Cl_2 , the *ee* is 90%, whereas that in MeCN is only 11%. Acetonitrile is the optimal solvent for ligands with two chiral centres such as **43e–n**. The researchers^{85,86} did not explain this fact. Apparently, the chiral centre of the dihydrooxazole ring in the compounds **43e–n** is responsible for the asymmetric induction because the diastereomers **43h** and **43l** provide *ee* of 90% and 93%, respectively, all other factors being the same.

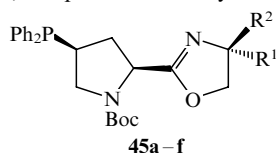
A number of phosphorus-substituted dihydrooxazoles **44a–m**, differing in the nature of the substituent R in the 2-position, have been synthesised.⁸⁷



R = Me (**a**), Bu^i (**b**), CHPh_2 (**c**), CPh_3 (**d**), 1-adamantyl (**e**), 3,5- $\text{Bu}_2\text{C}_6\text{H}_3$ (**f**), ferrocenyl (**g**), CF_3 (**h**), Ph (**i**), 4- MeOC_6H_4 (**j**), 4- MeC_6H_4 (**k**), 4- $\text{NO}_2\text{C}_6\text{H}_4$ (**l**), C_6F_5 (**m**).

These ligands ensure *ee* of up to 94% in the alkylation of dimethyl malonate with the allyl acetate **12** in the presence of $[\text{Pd}(\text{All})\text{Cl}]_2$, the compound **44e** being the most effective. Electron-donating substituents in the dihydrooxazole ring were found to increase the optical yield. In general, the enantioselectivity attained with the ligands **44a–m** is somewhat lower than that observed with the ligands **26a–t**. This was attributed⁸⁷ to the fact that the relative strain and the tendency for opening of the five-membered chelate metallacycles formed by the ligands **44** are

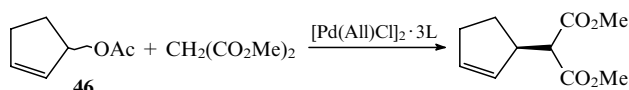
greater than those in the case of **26**. Indeed, according to ^{31}P NMR spectroscopy, the reaction of $[\text{Pd}(\text{All})\text{Cl}]_2$ with the compound **44k** taken in a twofold excess relative to the palladium complex results in a complex containing two organophosphorus ligands in the palladium coordination sphere, while the reaction of the compound **26e** with the same Pd complex yields a metallacycle with only one phosphorus-containing ligand. In view of these data together with the results obtained using the ligand **24**, one can formulate a general rule: the phosphorus-substituted dihydrooxazoles forming five-membered chelate metallacycles are less effective than those forming six-membered rings. In this connection, compounds **45a–f** synthesised recently⁸⁸ are worthy of note.



$\text{R}^1 = \text{H}$; $\text{R}^2 = \text{Pr}^i$ (**a**), Ph (**b**), Bu^t (**c**); $\text{R}^1 = \text{Pr}^i$; $\text{R}^2 = \text{H}$ (**d**);

$\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{H}$ (**e**); $\text{R}^1 = \text{R}^2 = \text{Me}$ (**f**).

For example, in the alkylation of dimethyl malonate with cyclopent-2-enyl acetate (**46**), *ee* reaches 96%, the yield of the final product being 79%–99%.



$\text{L} = \text{45a–f}$.

The optical yield and the absolute configuration of the reaction product are controlled by the pyrrolidine fragment because in the presence of the ligand **45f**, *ee* is only 80%. The ligands **45a–f** should form complexes containing seven-membered metallacycles, which are moreover rather strained; nevertheless, they ensure a high level of asymmetric induction. Thus, the enantioselectivity in this reaction does not depend on the size of the metal ring.

In addition to the two, to some extent, related processes, *i.e.*, allylic substitution and Heck reaction, phosphorus-containing dihydrooxazole P,N-bidentate ligands have found application in the asymmetric version of catalytic hydrosilylation. Thus the ligands **26a–c,f,i,k,o,r–t** have been studied in the reduction of a series of prochiral aromatic and aliphatic ketones with diphenylsilane {with $[\text{Rh}(\text{COD})\text{Cl}]_2$ as the pre-catalyst}.^{89,90} In the hydrosilylation of acetophenone, the degree of conversion is 80%–99% and the optical yield is up to 86%. The highest enantioselectivity was found for the ligands **26b** (*ee* 82%) and **26r** (*ee* 86%); the latter ligand, which contains electron-withdrawing substituents at the phosphorus centre ensures also the highest catalytic activity.⁹⁰ It should be noted that in the presence of the ligand **26c**, which displayed very good properties in allylic alkylation, *ee* is only 40%. Too bulky substituents at the phosphorus centre do not enhance the enantioselectivity. Indeed, with the ligand **26o**, *ee* is only 17%. It is noteworthy that the replacement of the PAr^1Ar^2 fragment in the compounds **26** by SPh or SePh almost eliminates the asymmetric induction.

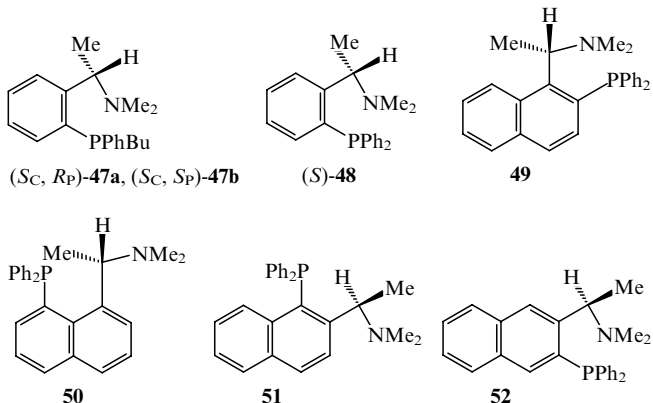
The use of the ligand **39** for the reduction of acetophenone with diphenylsilane {the catalytic system $[\text{Rh}(\text{COD})\text{Cl}]_2 \cdot 4\text{L}$ }⁹¹ proved especially successful (*ee* 94%). In the general case, the selectivity is inversely proportional to the size of the substituent at the 4-position of the dihydrooxazole fragment of the ligand. However, the asymmetric induction provided by the ligand **39** was found to be abnormally high, despite the fact that the two methyl substituents in the compound **39** create greater steric hindrance than one *tert*-butyl substituent in the compound **26c**. In the opinion of the investigators cited,⁹¹ interpretation of these effects requires further research into the mechanism of the rhodium-catalysed hydrosilylation and the structure of intermediates.

IV. Other groups of chiral P,N-bidentate ligands

The two classes of optically active P,N-bidentate ligands considered above mainly include particular series of compounds prepared specially to be investigated in catalytic reactions. The other compounds used as P,N-bidentate ligands are difficult to classify because they belong to different classes and types. We classified these compounds in terms of the structures of the nitrogen and phosphorus electron-donating centres; three groups of ligands were thus distinguished. Within each group, the data are mainly arranged according to the type of the catalytic reaction.

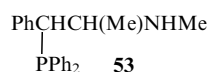
1. Ligands with sp^3 -hybridised electron-donating nitrogen atoms

Chiral P,N-bidentate ligands with sp^3 hybridised electron-donating nitrogen atoms became known earlier than other compounds (except for aminoalkylferrocenylphosphines). Back in 1977, syntheses of compound **47a** with two asymmetric centres, carbon and phosphorus, and the complex of the phosphine **47a** with PdCl_2 were reported.⁹² The formation of the metal chelate ring and the absolute configuration of the chiral centres in the complex were proved by X-ray diffraction analysis. Subsequently,⁹³ several more aminophosphines with benzene or naphthalene nuclei have been reported, for example, (*S*)-AMPHOS **48**, 1,2-DPNEA **49**, 1,8-DPNEA **50**, 2,1-DPNEA **51** and 2,3-DPNEA **52**.

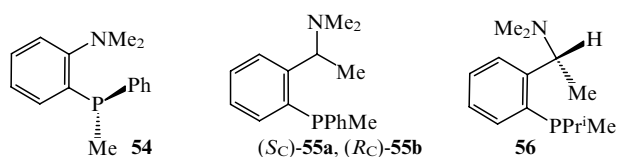


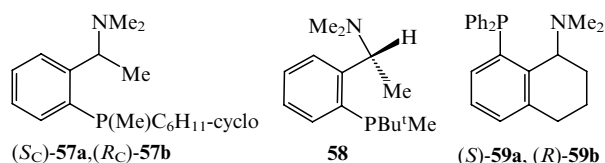
Neutral or cationic Rh(I) complexes with ligands of the type **47b** and **48–51** were used as catalysts of hydrogenation of prochiral unsaturated acids. Thus hydrogenation of itaconic acid in the presence of 1,2-DPNEA **49** proceeds with an optical yield of up to 43%.⁹³

Other ligands, for example, the phosphorus-containing ephedrine derivative **53**, have also found application in the hydrogenation of prochiral unsaturated acids. The reduction of *N*-acetyl- α -aminocinnamic acid in the presence of $[\text{Rh}(\text{C}_8\text{H}_{14})\text{Cl}]_2$ and the ligand **53** gives the product in an optical yield reaching 77%.⁹⁴

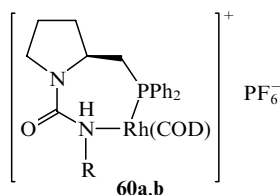


Ligands **54**, **55a,b**, **56**, **57a,b**, **58** and **59a,b**^{95,96} have been used in the hydrogenation of *N*-acetyl- α -aminocinnamic and *N*-benzoyl- α -aminocinnamic acids in the presence of $[\text{Rh}(\text{C}_6\text{H}_8)\text{Cl}]_2$. The maximum optical yield (68%) was attained in the case of (*S*)-1-[2-(methyl-*tert*-butylphosphino)phenyl]ethylamine (**58**).⁹⁶



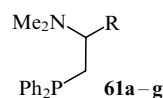


The cationic rhodium(I) complexes **60a,b** have been synthesised and characterised in detail by ¹H, ³¹P and ¹³C NMR and IR spectroscopy and conductometry.⁹⁷ The ligands present in these complexes contain rarely encountered carbamide donor centres. However, the reduction of Z-(α)-ethylacetaminocinnamic acid in the presence of the complex **60b** resulted in only a moderate enantioselectivity (*ee* 34%).

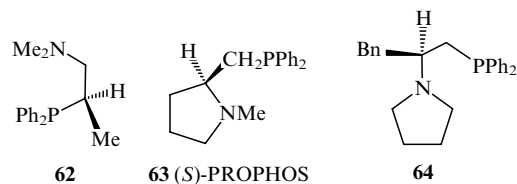


R = Bu^t (**a**), (CH₂)₃Si(OEt)₃ (**b**).

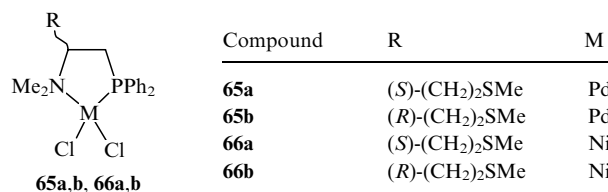
Yet another traditional field of application of chiral amino-phosphines with an *sp*³-hybridised nitrogen atom is cross-coupling. Both acyclic (**61a–g**, **62**) and heterocyclic (**63**, **64**) aminophosphines have been employed in these reactions.^{98,99}



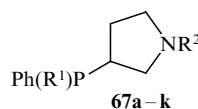
Compound 61	R	Abbreviation
a	Me	(S)-ALAPHOS
b	Pr ⁱ	(S)-VALPHOS
c	Bu ⁱ	(S)-LEUPHOS
d	Bu ^t	(R)-t-LEUPHOS
e	Ph	(R)-PhGLYPHOS
f	Bn	(S)-PHEPHOS
g	cyclo-C ₆ H ₁₁	(R)-ChGLYPHOS



Cross-coupling of 1-phenylethylmagnesium chloride with vinyl bromide in the presence of complexes of PdCl₂ with the ligands **61a–g**, **62**, **63** and **64** proceeds with a moderate enantioselectivity [*ee* up to 55% for (S)-PHEPHOS **61f**]. The catalytic system NiCl₂·L was found to be more efficient; indeed, in the case of the ligand **61d**, the optical yield reaches 94%. It should be noted that movement of the chiral centre towards the phosphorus atom results in a decrease in the asymmetrising activity (*ee* 38% for **61a** and *ee* 25% for **62**).⁹⁹ For example, in the cross-coupling of 1-phenylethylmagnesium chloride with β-bromostyrene, the Ni complex (S)-AMPHOS **48** exhibits no catalytic effect, while PdCl₂·[(S)-AMPHOS] ensures a 95% chemical yield and a 40% optical yield.¹⁰⁰ Palladium(II) *cis*-dichloro compounds **65a,b** have been synthesised and characterised by X-ray diffraction data.¹⁰¹ These complexes and nickel complexes **66a,b** having a similar structure were tested in the cross-coupling of 1-phenylethylmagnesium chloride with vinyl bromide. In the presence of the palladium complexes **65a,b**, the optical yield was moderate (*ee* up to 45%). The use of the nickel complexes **66a,b** resulted in a higher enantioselectivity (for **66b**, *ee* 88%).



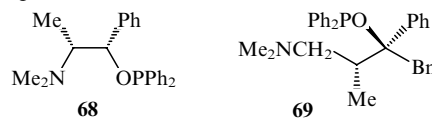
The synthesis of P,N-bidentate ligands **67a–k**, containing a pyrrolidine ring, has been described.^{102,103}



Compound 67	R ¹	R ²
a	Ph	H
b	Ph	Bn
c	Ph	2-MeOC ₆ H ₄ CH ₂
d	Ph	Et
e	H	H
f	2-MeOC ₆ H ₄ CH ₂	H
g	2,4,6-(MeO) ₃ C ₆ H ₂ CH ₂	H
h	2-MeOC ₆ H ₄ CH ₂	Bn
i	2,4,6-(MeO) ₃ C ₆ H ₂ CH ₂	Bn
j	H	Bn
k	H	Ph

The compounds **67b,c,g,h,i** were used to prepare the *cis*-diiodo metal chelates PdI₂·L, having a heteronorborene skeleton; diastereomeric palladium complexes with the ligands **67a–g** were separated by column chromatography. The structure of the complex compounds was convincingly proved by IR spectroscopy and ¹H, ¹³C and ³¹P NMR spectroscopy (including the use of solid-state techniques), FAB mass spectrometry and X-ray diffraction analysis. However, these products were not selective in cross-coupling, the *ee* values being not more than 10%. Meanwhile, in the case of NiCl₂·**67b**, the chemical yield is 98% and the optical yield is 75%.¹⁰³

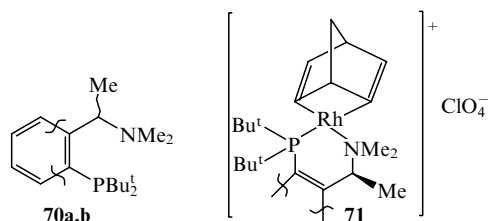
P,N-Bidentate ligands **68** and **69**, containing a phosphinite group, have been described.¹⁰⁴



Palladium complexes formed by the ligands **68** and **69** proved to be inefficient in the cross-coupling of 1-phenylethylmagnesium bromide with vinyl bromide; the optical yield was only 6%–9% for a degree of conversion of 60%–74%.¹⁰⁴ This outcome was explained by insufficient rigidity of six- and seven-membered palladacycles and by lower basicity of the phosphinite group in comparison with the phosphine group. However, this interpretation is quite debatable. The palladium complexes were characterised only by ³¹P and ¹H NMR spectra. No data of long-wavelength IR spectroscopy which would provide information on the arrangement of the chloro ligands at the Pd atom based on the position of the ν_{Pd–Cl} band are available. No data on the molecular masses of the complexes can be found either. Therefore, it cannot be ruled out that the reaction of the ligand **69** with PdCl₂ gives a bi- or poly-nuclear compound [PdCl₂·L]_n, in which the P,N-bidentate ligands function as bridges linked according to the 'head-to-tail' pattern, rather than a chelate. As regards the basicity of the phosphorus centre in cross-coupling catalysts, the statistical data available to date do not permit an unambiguous conclusion about its role in the enantioselectivity. It is quite probable that in the case of aminophosphinites **68** and **69**, an appropriate catalytic system has not been chosen.

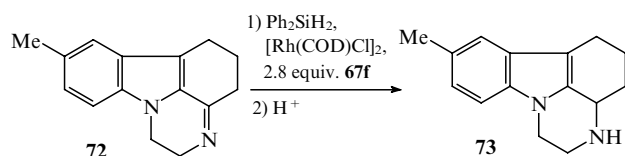
Several chiral aminophosphines have been tested in asymmetric hydrosilylation. For instance, the reduction of acetophenone with diphenylsilane with participation of (*S*)-AMPHOS **48** {[Rh(C₂H₄)₂Cl]₂ as the pre-catalyst} gave the corresponding alcohol with *ee* 33%, and in the case of reduction of *tert*-butyl methyl ketone, *ee* was 72%.¹⁰⁵ Subsequently,¹⁰⁶ this result was somewhat improved: catalysis by [Rh(COD)Cl]₂·10L, where L = (*S*)-AMPHOS **48**, gave α -phenylethyl alcohol in an optical yield of 51% and a chemical yield of 97%. Other pre-catalysts proved to be less efficient: for Pd(COD)Cl₂, *ee* reaches 50.5% but the degree of conversion is only 13%, while for Pt(COD)Cl₂ and [Ir(COD)Cl]₂, *ee* does not exceed 27%.

It should be noted that close analogues of (*S*)-AMPHOS **48** containing a di(*tert*-butyl)phosphine group in the benzene ring, instead of the diphenylphosphine group, are known,¹⁰⁷ namely, (*S*)- (**70a**) and (*R*)-DIBUTPHOS **70b**. According to X-ray diffraction analysis,¹⁰⁷ in the rhodium complex **71**, the ligand (*R*)-DIBUTPHOS **70b** forms a metal chelate.



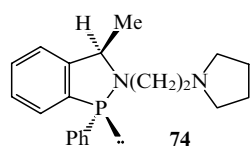
However, the use of the ligands **70a,b** in the hydrosilylation of acetophenone with phenyldimethylsilane {with [Rh(C₂H₄)₂Cl]₂ as the pre-catalyst} gave a quite unexpected result: for a chemical yield of up to 92%, no enantioselectivity was observed at all.

The ligand (*S*)-PHEPHOS **61f** ensures an optical yield of 54% in the hydrosilylation of acetophenone with diphenylsilane {the [Rh(COD)Cl]₂·4L system}.¹⁰⁸ When cyclic imine **72** was subjected to hydrosilylation with diphenylsilane in the presence of the [Rh(COD)Cl]₂·2.8L system, where L = (*S*)-PHEPHOS **61f**, compound **73**, the enantiomer of the antidepressant pyrazidol, was obtained in 69% yield and *ee* 73%.¹⁰⁹



The behaviour of (*S*)-PHEPHOS **61f** and (*S*)-AMPHOS **48** in the reaction with [Rh(COD)Cl]₂ and [Rh(CO)₂Cl]₂ has been studied.¹¹⁰ The reaction products, binuclear Rh(I) complexes of the [Rh(L)Cl]₂ type and mononuclear complexes of the Rh(CO)Cl(L) type, were isolated and characterised by spectroscopy (IR, X-ray electron, ¹H NMR, ³¹P NMR and mass spectra).

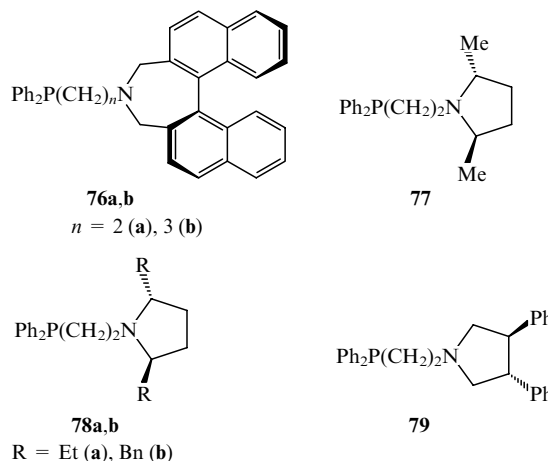
To summarise the foregoing, it should be noted that rhodium and palladium derivatives of chiral aminophosphines with an *sp*³-hybridised peripheral nitrogen atom provide moderate enantioselectivity as catalysts of hydrogenation, cross-coupling and hydrosilylation. However, they are more effective in allylic substitution. Specifically, amino-substituted phosphinous amide **74**, in which the asymmetric phosphorus atom is incorporated in a heterocycle, ensured a chemical yield of 99% and an optical yield of 62% in the alkylation of dimethyl malonate with the acetate **12** {with [Pd(All)Cl]₂ as the pre-catalyst}.¹¹¹



The same model reaction was used to test a series of amino phosphinous amides **75a–j**, in which the phosphorus atom is achiral {[Pd(All)Cl]₂ as the pre-catalyst}.¹¹² In the presence of these ligands, *ee* is 76% for a chemical yield of 41%–82%. The best optical yield was attained with the ligand **75h**, having no substituents at the amide nitrogen atom.

Compound 75	R ¹	R ²
a	H	H
b	Me	Me
c	Bn	Bn
d	Pr ⁱ	Pr ⁱ
e	CH ₂ CH ₂ Pr ⁱ	CH ₂ CH ₂ Pr ⁱ
f	2-MeC ₆ H ₄ CH ₂	2-MeC ₆ H ₄ CH ₂
g	3-MeC ₆ H ₄ CH ₂	3-MeC ₆ H ₄ CH ₂
h	Bn	H
i	2-MeC ₆ H ₄ CH ₂	H
j	Bu ^t CH ₂	H

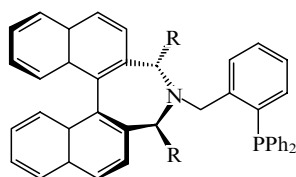
Ligands **76a,b**, **77**, **78a,b** and **79** with axial or central chirality of the peripheral nitrogen atom have been prepared.¹¹³



In the model allylic alkylation using [Pd(All)Cl]₂ as the pre-catalyst, the use of the ligands **76a,b** results in *ee* values of 93% and 96%, respectively. The chemical yields are 96%. An increase in the optical yield on passing from the compound **76a** to **76b**, was attributed¹¹³ to an increase in the size of the chelate metallacycle it forms. The ligands **77**, **78a,b** and **79** are much less enantioselective (*ee* up to 39%). In the presence of the ligands **80a–c**, in which the phosphorus center is further removed from the nitrogen centre, the asymmetric induction decreases with an increase in the distance between the donor centres.¹¹³

Compound 80	<i>n</i>	<i>m</i>
a	1	0
b	2	0
c	1	1

In the alkylation of dimethyl malonate with the acetate **12**, the ligands **80a–c** [with Pd(OAc)₂ as the pre-catalyst] ensure *ee* of 96%, 79% and 18%, respectively.¹¹⁴ The low optical yield observed in the last-mentioned case was explained by assuming monodentate coordination of the compound **80c** for the formation of the intermediate. The ligands **80a–c** were also employed in the cross-coupling of (1-phenylethyl)magnesium chloride with vinyl bromide. The best result (*ee* 46%) was observed for the ligand **80b**; in other cases, *ee* did not exceed 9%. Compounds **81a,b**, having a similar structure and containing additional chiral centres in the dihydroazepine ring, offer no advantages over the ligands **80a–c**.¹¹⁵



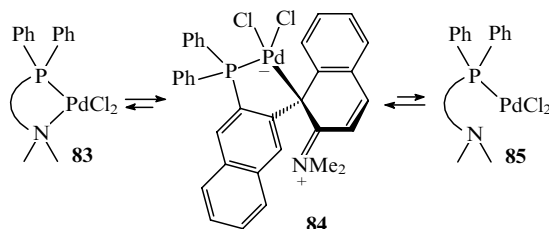
81a,b [R = Me (a), Et (b)]

In the same model allylic alkylation reaction {with [Pd(All)Cl]₂ as the pre-catalyst}, *ee* is 59% for the ligand **81a** and 37% for the ligand **81b**. A higher enantioselectivity (*ee* 68%) was achieved in the alkylation of dimethyl malonate with the sterically less shielded acetate **13** {the [Pd(All)Cl]₂ · **81a** catalytic system}.

When dinaphthalene derivatives **82a–h**, which also have a chiral axis, are employed in allylic alkylation [the acetate **12**, pre-catalyst Pd(dba)₂], the chemical yields are 77%–95% and the optical yields are 53%–73% (the ligand **82f** is the most effective).

Compound 82	R ¹	R ²
a	H	H
b	Me	Me
c	H	Et
d	H	Pr ⁱ
e	H	cyclo-C ₆ H ₁₁
f	Me	Pr ⁱ
g	Me	cyclo-C ₆ H ₁₁
h	cyclo-C ₆ H ₁₁	cyclo-C ₆ H ₁₁

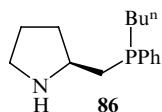
The reaction of aminophosphine **82b** with PdCl₂(PhCN)₂ has been studied.¹¹⁶ According to the ¹H, ¹³C and ³¹P NMR spectra, the reaction gives an equilibrium mixture of three complexes, **83**, **84** and **85**, in a ratio of 10:85:5.



It was demonstrated by X-ray diffraction analysis that the complex **84**, which predominates in the mixture, is a chelate formed due to the P–C_σ binding. It was noted that this type of binding can play an essential role in the formation of intermediates in allylation processes.

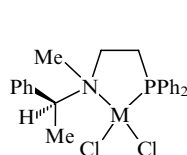
Chiral N-*sp*³-hybridised aminophosphines, which have not yet found application in catalysis but, in our opinion, hold considerable promise, deserve special consideration. Most of these compounds contain asymmetric phosphorus and/or nitrogen atoms.

In particular, the reaction of compound **86** with PdCl₂(MeCN)₂ results in two epimers of the palladium chelate complexes, PdCl₂·[(S_N, S_C, S_P)-**86**] and PdCl₂·[(S_N, S_C, R_P)-**86**], which were separated by fractional crystallisation.¹¹⁷

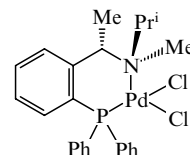


Palladium and platinum *cis*-dichloro complexes **87a,b** with two chiral centres have also been described.¹¹⁸

Whereas the platinum complex **87a** exists as a single diastereomer (the asymmetric nitrogen atom has only one config-



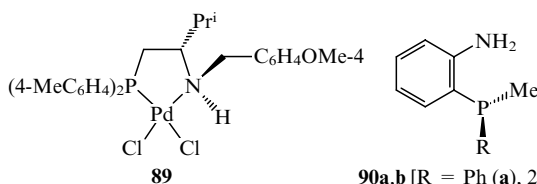
87a,b [M = Pt (a), Pd (b)]



88

uration), the palladium analogue **87b** undergoes epimerisation with a half-transformation period of 30 min (according to ¹H NMR spectra and polarimetry). Unlike the complex **87b**, compound **88** contains a configurationally stable chiral nitrogen centre due to the stereochemical assistance of the neighbouring endocyclic carbon centre.¹¹⁹

The chiral nitrogen centre in the compound **89** also possesses configurational stability, as shown¹²⁰ by the data of ¹H (2D NOESY), ¹³C, ¹⁵N and ³¹P NMR, IR and mass spectra and X-ray diffraction analysis.

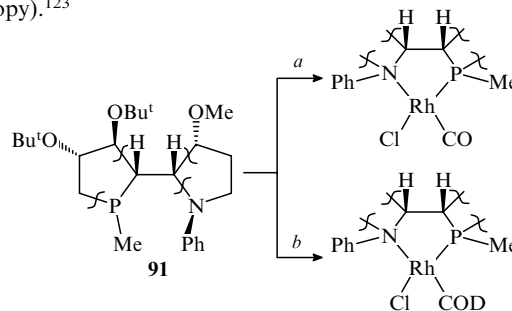


90a,b [R = Ph (a), 2-ClC₆H₄ (b)]

The complex exists as a single diastereomer both in solution and in the solid state but the palladacycle retains configurational mobility. The conformers differ little in energy, which detracts from the potential use of the compound **89** as a ligand in stereoselective catalysis.

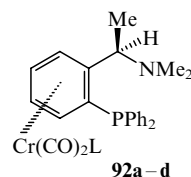
Some aminophosphines with chiral centres at the phosphorus atom also appear interesting, for example, compounds **90a,b**, for which both neutral and cationic palladium(II) chelates have been obtained.^{121, 122}

The original bicyclic compound **91** contains five asymmetric carbon atoms in addition to the chiral phosphorus atom. This compound can bind to a metal as both a P-monodentate or a P,N-bidentate ligand (according to ³¹P, ¹³C and ¹H NMR spectroscopy).¹²³



(a) 0.5 equiv. [Rh(CO)₂Cl]₂; (b) 0.5 equiv. [Rh(COD)₂Cl]₂.

The complex PdBr(R)(L), where L = (*R*)-AMPHOS [(*R*)-**48**], R = Me, C ≡ CSiMe₃, has been synthesised.¹²⁴ Several ligands **92a–d** based on (*R*)-AMPHOS [(*R*)-**48**] have been prepared.¹²⁵



92a–d

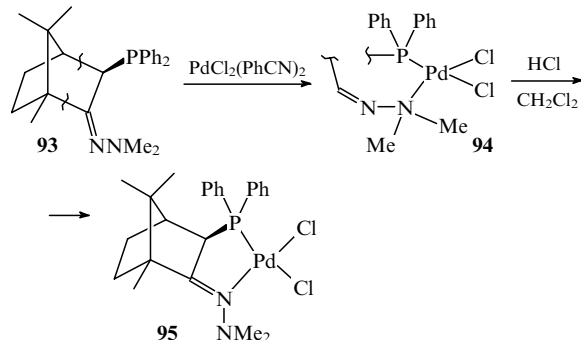
L = CO (a), PPh₃ (b), P(OMe)₃ (c), P(OPh)₃ (d).

The complexes **92a–d** have found application so far only in the amination of 4-bromotoluene with piperidine catalysed by

palladium complexes; however, they are also of interest for asymmetric synthesis, especially in view of the possibility of changing the electronic properties of the phosphorus centre by changing the nature of the ligand L.¹²⁵

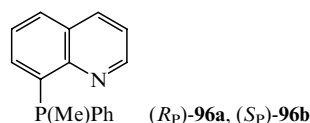
The dimethylhydrazone of the phosphorus-substituted (*R*)-camphor **93** reacts with $\text{PdCl}_2(\text{PhCN})_2$ to give initially six-membered chelate metallacycle **94** (according to the IR spectra, ^{31}P and ^1H NMR spectra and X-ray diffraction analysis).¹²⁶

On treatment of a solution of the complex **94** in CH_2Cl_2 with dry hydrogen chloride, the metal chelate rearranges giving rise to complex **95** with a coordinated sp^2 -hybridised nitrogen atom.



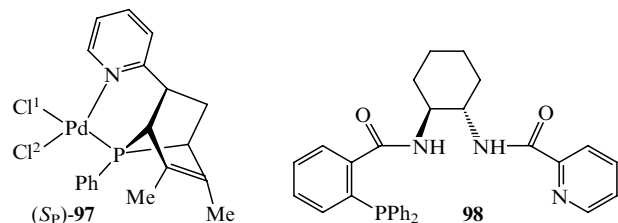
2. Ligands with sp^2 -hybridised electron-donating nitrogen atoms

The interest in ligands with sp^2 -hybridised donor nitrogen atoms arose somewhat later than that in compounds with sp^3 -hybridised nitrogen centres. In 1982, phosphines **96a,b** and their neutral palladium derivatives $\text{PdCl}_2(\text{L})$ were synthesised.¹²⁷ Later,¹²⁸ the cationic complexes $[\text{Pd}(\text{L})_2]^{2+}(\text{PF}_6^-)_2$ and $[\text{PdCl}(\text{L})]^{+}\text{X}^{-}$ ($\text{X} = \text{Cl}, \text{PF}_6$) were prepared.

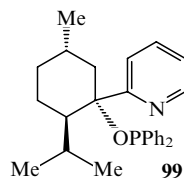


Several other fairly interesting ligands and complexes based on them, for example, **97–99**, have been reported.^{129–131} X-ray diffraction analysis¹²⁹ showed that the $\text{Pd}-\text{Cl}(1)$ bond length in the complex **97** [2.394(2) Å] is markedly greater than the typical value, due to the strong *trans*-effect of the phosphorus centre with an unusual geometry.

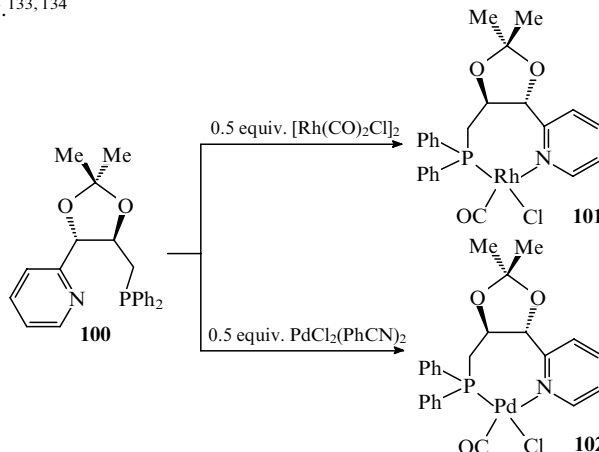
The ligand **98** has a nine-atom bridge between phosphorus and nitrogen. It is thus able to form 12-membered macrometallacycles.¹³⁰ Nevertheless, the enantioselectivity (*ee* 86%) in the model alkylation of dimethyl malonate with the allyl acetate **12** {with $[\text{Pd}(\text{All})\text{Cl}]_2$ as the pre-catalyst} is quite comparable with the enantioselectivity attained when using catalysts with a standard size of the chelate ring.



Cationic complexes of the phosphinite **99**, $[\text{Rh}(\text{CO})_2(\text{PPh}_3)(\text{L})]^+\text{ClO}_4^-$ and $[\text{Rh}(\text{COD})(\text{L})]^+\text{ClO}_4^-$ (the latter was studied by X-ray diffraction analysis), have found use as catalysts of hydroformylation of a number of unsaturated substrates such as vinyl acetate, styrene, vinyl naphthalene and methyl acrylate.¹³¹ The optical yields were 12%, 6%, 78% and 92%, respectively for rather high degrees of conversion and regioselectivities. However, later it was shown¹³² that the last-mentioned value was erroneous.

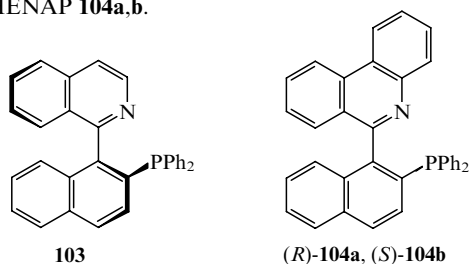


The formation of complexes by phosphine **100** (PYDIPHOS) was thoroughly studied by spectral methods (IR spectroscopy, ^{31}P , ^1H and ^{13}C NMR spectroscopy) and mass spectrometry.^{133, 134}

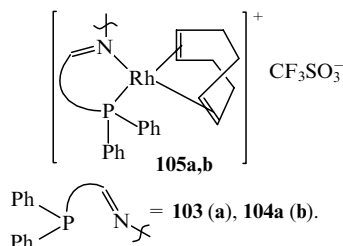


Both rhodium (**101**) and palladium (**102**) metal complexes were described as chelates (the structure of the complex **102** was confirmed by X-ray diffraction analysis); however, the data obtained for the complex **101** do not rule out unambiguously an alternative highly symmetrical binuclear structure with bridging coordination of the P,N-bidentate ligands of the 'head-to-tail' type.¹³⁴ The enantioselectivity observed in catalytic reactions involving PYDIPHOS (**100**) is moderate. For hydroformylation of styrene in the presence of the complex **101**, the *ee* is 28%; ethoxycarbonylation in the presence of the complex **102** results in *ee* of 20%; in the model allylic alkylation {the $[\text{Pd}(\text{All})\text{Cl}]_2 \cdot 4\text{L}$ system}, *ee* is 9%.¹³⁵

Studies by Brown *et al.*^{136–141} deserve special attention. These researchers proposed effective ligands QUINAP **103** and PHENAP **104a,b**.

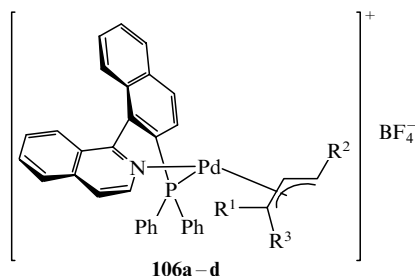


Cationic rhodium complexes **105a,b** with these ligands have found successful use as catalysts of hydroboration of vinylarenes with catecholborane.^{137, 138} The optical yields were 64%–95% and the chemical yields were 21%–71%. For example, in the hydroboration of styrene in the presence of the complexes **105a,b**, the *ee* values were 91% and 67%, respectively.¹³⁸



The complex **105a** has also been used as the catalyst for hydroboration–amination of vinylarenes;¹³⁹ the corresponding primary amines were obtained in optical yields of 77%–98% and in chemical yields of 50%–64%.

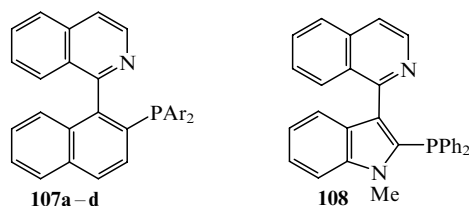
Allylic palladium complexes **106a–d** with the P,N-bidentate ligand **103** have been synthesised. Their structure was established based on the spectral data (IR spectroscopy and ³¹P, ¹³C and ¹H NMR spectroscopy and mass spectrometry).¹⁴⁰



Compound 106	R ¹	R ²	R ³
a	H	H	H
b	Ph	H	H
c	Ph	Ph	H
d	Ph	Ph	Ph

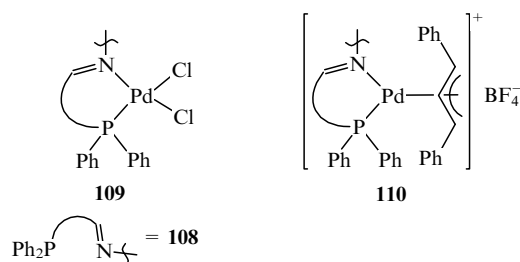
In the classical alkylation of dimethyl malonate with the allyl acetate **12** catalysed by the complex **106a**, the optical yield fluctuates from 67% to 98%, depending on the reaction conditions. For other allylic substrates, the optical yield varies from 47% to 67%. The replacement of dimethyl malonate by diethyl malonate decreases somewhat the enantioselectivity (*ee* 75%–78%). The use of the neutral complex PdCl₂·**103** instead of the cationic complex **106a** increases the optical yield (*ee* 79%).¹⁴⁰ A similar complex in which [Pd(All)(**104a**)]⁺ BF₄[−] is used instead of QUINAP **103** ensures a commensurable level of asymmetric induction in this reaction (*ee* 95%).¹⁴¹

Ligands **107a–d**¹⁴² used in hydroboration and compound **108**¹⁴³ containing an indole fragment have been prepared recently.



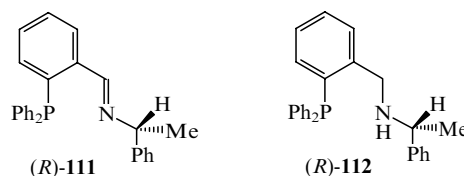
Compound 107	Configuration	Ar
a	<i>S</i>	3-MeC ₆ H ₄
b	<i>S</i>	3,5-Me ₂ C ₆ H ₃
c	<i>R</i>	2-biphenyl
d	<i>R</i>	2-furyl

Unfortunately, both the ligand **108** itself and its complex with PdCl₂ **109** are readily racemised. The corresponding cationic allylpalladium complex **110** is the only diastereomer.

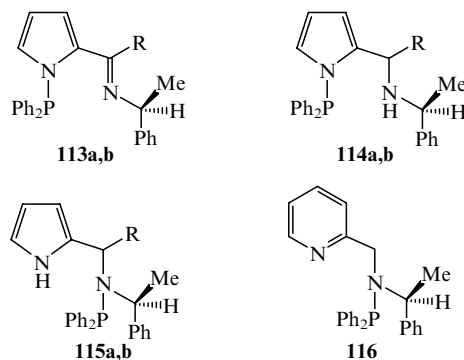


The structures of **109** and **110** were studied¹⁴³ using spectral methods (IR and ³¹P, ¹H and ¹³C NMR spectroscopy and mass spectrometry). The complex **110** was studied by X-ray diffraction analysis. The metal atoms in both complexes were found to be coordinated to the isoquinoline nitrogen atom. The configurational stability of the allylic cationic complexes of Pd(II) of the type **110** gives hope for their successful use in asymmetric allylic substitution.¹⁴³

In addition to ligands with a pyridine or isoquinoline fragment, a large group of ligands with a peripheral imino group, iminophosphines, have been described. They were studied by Brunner *et al.*^{144, 145, 148–150} In particular, (*R*)-IMINPHOS **111** and (*R*)-AMINPHOS **112** (prepared by the reduction of **111** with NaBH₄) were compared in the hydrogenation of *N*-acetyl-α-aminocinnamic acid {[Rh(C₂H₄)₂Cl]₂ as the pre-catalyst} and hydrosilylation of acetophenone with diphenylsilane {[Rh(COD)Cl]₂ as the pre-catalyst}.¹⁴⁴



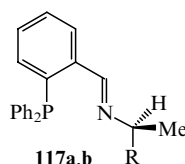
The ligand (*R*)-**111** was more enantioselective in hydrogenation than (*R*)-**112** (*ee* 17% and 14%, respectively). The *ee* value attained in hydrosilylation is 29% in the presence of (*R*)-IMINPHOS **111** and 53% for (*R*)-AMINPHOS **112**.¹⁴⁴ Note that the ferrocene arylideneaminophosphines **17a–d** and the aminophosphines (*S,R*)-**18** exhibit a diametrically opposite pattern of dependence (see Section II.2.b). Subsequently,¹⁴⁵ other imino- and amino-phosphines such as **113a,b**–**115a,b** and **116** have been studied in the hydrosilylation of acetophenone {[Rh(COD)Cl]₂ as the pre-catalyst}; however, they all proved to be middling asymmetric inducers because they ensured *ee* of not more than 20%. The best results were obtained with the ligands **113a** and **115a**.



R = H (**a**), Me (**b**).

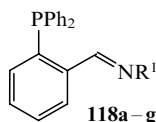
A later publication¹⁴⁶ describes the synthesis of the (*S*)-enantiomer of IMINPHOS [(*S*)-**111**] and a large series of its palladium and platinum complexes such as PdCl(Me)(L), [Pd(η³-All)(L)]⁺ X[−] (η³-All = 2-RC₃H₄, 2-MeC₃Me₄, 2-RC₃H₂Me₂; X = Cl, O₃SCF₃), PdCl₂(L).¹⁴⁹ The chelating P,N-bidentate coordination of the ligand in these complexes was proved by ³¹P, ¹H and ¹³C NMR spectroscopy; neutral Pd(II) complexes were studied by X-ray diffraction analysis.

Close analogues of IMINPHOS **111**, compounds **117a,b**, are also known.¹⁴⁷ The enantioselectivity exhibited by these compounds in the alkylation of dimethyl malonate with the allyl acetate **12** catalysed by Pd complexes is also low (*ee* does not exceed 17%).

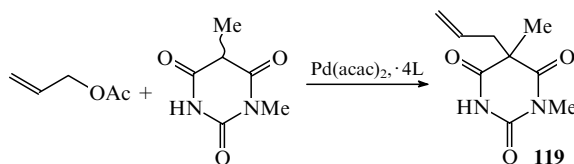
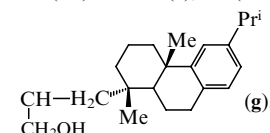


R = cyclo-C₆H₁₁ (**a**), 2-naphthyl (**b**).

Quite recently, a new large series of iminophosphines **118a–g** have been proposed;^{148–150} these products were used to prepare biologically active compound **119**, which belongs to the group of barbiturates.¹⁴⁹ In the reaction catalysed by palladium acetylacetonate in the presence of (*S*)-**118e**, the yield of the compound **119** was 89% (*ee* ~ 34%).

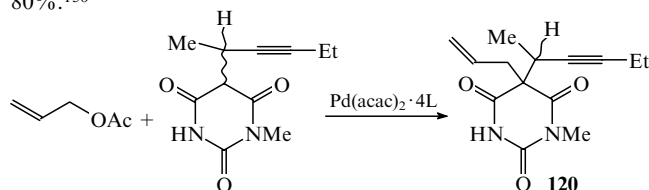


R¹ = C(Ph)(Me) (**a**), HC(Me)CH₂OH (**b**), HC(Et)CH₂OH (**c**), HC(Prⁱ)CH₂OH (**d**), HC(Bu^t)CH₂OH (**e**), HC(Ph)CH₂OH (**f**),



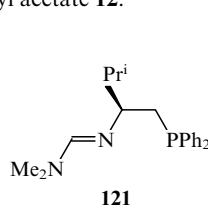
L = (*S*)-**118e**.

Although the optical yield attained is relatively low, this reaction opens up the way for accumulation of a valuable medicinal preparation, namely, the anesthetic methohexital **120**, which was prepared in the presence of the ligand (*S*)-**118e** in an optical yield of 80%.¹⁵⁰

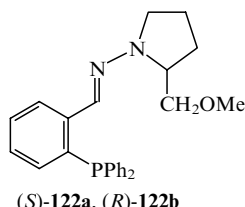


L = (*S*)-**118e**.

Chiral aminoiminophosphines **121** and **122a,b** were found to be fairly effective in the alkylation of dimethyl malonate with the allyl acetate **12**.^{151–153}



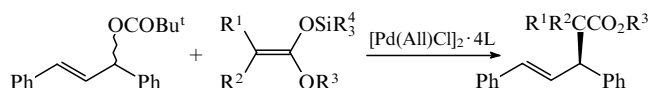
121



(*S*)-**122a**, (*R*)-**122b**

When the reaction was carried out with the ligand **121** {[Pd(All)Cl]₂ as the pre-catalyst}, the chemical yield was 85% and the optical yield was 92%. In the allylic palladium intermediate, the ligand was found¹⁵¹ to be coordinated through the phosphorus atom and the imine nitrogen atom. The iminophosphines **122a,b** are also effective in this reaction {[Pd(All)Cl]₂·3L as the catalyst}: *ee* is 90%–92% for a nearly quantitative chemical yield.¹⁵² The ligand **121** was used in processes in which ketene silyl

acetals are used as nucleophiles.¹⁵³ The yields in these reactions reach 95% and *ee* is 93%.

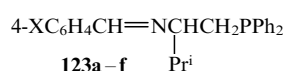


R¹ = R² = R³ = R⁴ = Me; R¹–R² = (CH₂)₅; R³ = R⁴ = Me;

R¹ = R² = H, R³ = Me, R⁴ = Bu^tMe₂; R¹ = CO₂Me, R² = H,

R³ = R⁴ = Me; L = **121**.

Recently, a new series of phosphorus-substituted imines **123a–f**, containing substituents of different nature in the arylmethylidene fragment, have been prepared.¹⁵⁴ In the alkylation of dimethyl malonate with 3-pivaloyloxy-1,3-diphenylprop-1-ene {catalysed by [Pd(All)Cl]₂·4L}, the catalytic activity was found to be directly correlated with the enantioselectivity, on the one hand, and the electron-donating capacity of the substituent X on the other hand.



Compound 123	X	Yield (%)	<i>ee</i> (%)
a	CO ₂ Me	42	19
b	CF ₃	46	38
c	H	57	52
d	Me	76	74
e	OMe	88	85
f	NMe ₂	99	92

In the author's opinion,¹⁵⁴ this is due to the increase in the stability of the Pd(II) cationic complexes on passing from the ligand **123a** to **123f**.

It should be noted that ligands with *sp*²-hybridised donor nitrogen atoms have made a greater contribution to asymmetric catalysis than the ligands with *sp*³-hybridised nitrogen because, in addition to allylic alkylation, they are effective in hydroboration–oxidation and hydroboration–amination processes.

3. P,N-Bidentate derivatives of phosphorous acid

About 250 chiral P,N-bidentate ligands are currently used in the synthesis of coordination compounds and in asymmetric catalysis. The natures of the nitrogen centres in these compounds are quite diverse, while the phosphorus centres are usually acyclic phosphines (a PAr₂ fragment is encountered most often). (Phosphinites such as **42**, **68**, **69** and **99** and phosphinous amides **74** and **113–116** are the scanty exceptions.) The introduction of electron-donating or electron-withdrawing substituents into the corresponding positions of the benzene nucleus is almost the only method of controlling the inductive effect of phosphorus. However, there exists another, more effective method different in kind, namely, replacement of the carbon atoms in the first coordination sphere of phosphorus by heteroatoms (oxygen and/or nitrogen). This method allows fine adjustment of the chemical stability, the donor–acceptor properties and steric requirements of the ligand. A phosphorus centre of this type is present in P,N-bidentate ligands derived from phosphorous acid.

It is noteworthy that, starting from the early 1990s, the number of publications devoted to the use of chiral phosphites and phosphorous amides, especially P,P-bidentate ones, in the coordination chemistry and catalysis, has substantially increased.^{155, 156} The obvious advantages of these ligands have been outlined.¹⁵⁷

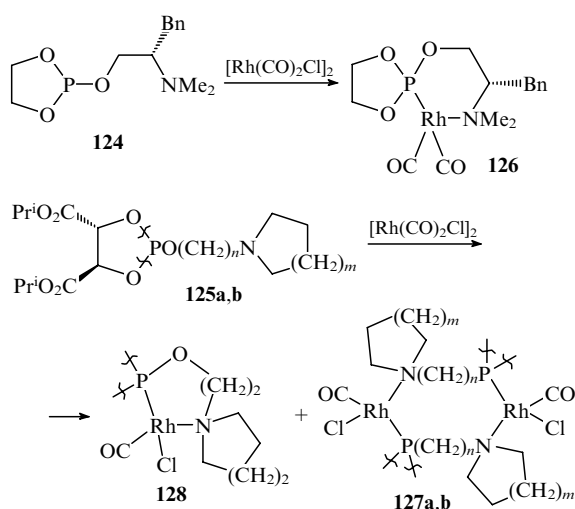
(i) They are readily available because most of them, including functionally substituted ones, can be prepared fairly easily (in one or two steps) and in a high yield from widely used optically active organic precursors, for example, amino alcohols or diols.

(ii) No P–C bonds, which would considerably hamper the oxidative destruction of the ligand, are present in the molecule.

(iii) Owing to the clear-cut π -acceptor properties inherent in phosphites,¹⁵⁸ they are more electrophilic ligands; coordinated phosphites are able to stabilise low oxidation states of complex-forming metals.

It should be noted that chiral phosphinophosphites are the best ligands for asymmetric hydroformylation.^{132,156} The introduction of an N-donor centre into the molecule of an ester or an amidoester of phosphorous acid extends the scope of application of chiral phosphites.

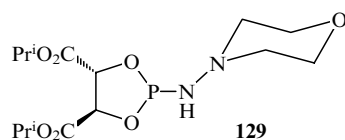
The first publication reporting the synthesis and complex formation of optically active aminoalkyl phosphites **124** and **125a,b** appeared in 1993.¹⁵⁹ The reaction of the compounds **124** and **125** with $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ afforded mono- and bi-nuclear Rh(I) chloro carbonyl complexes.^{159,160} The ligand **124** forms metal chelate **126**, while the ligand **125b** gives dimer **127b**. The reaction of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with the ligand **125a** gives rise to a mixture of monomer **128** and dimer **127a**; during storage of the solution, the latter product gradually rearranges to complex **128**. It should be noted that the complexes **127a,b** and **128** have been studied only in solution.



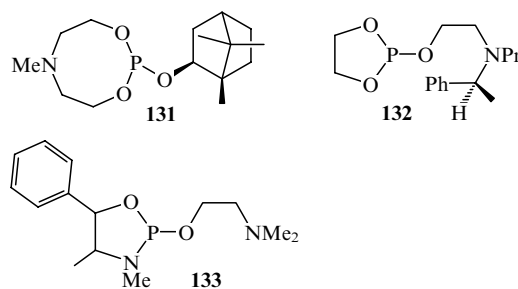
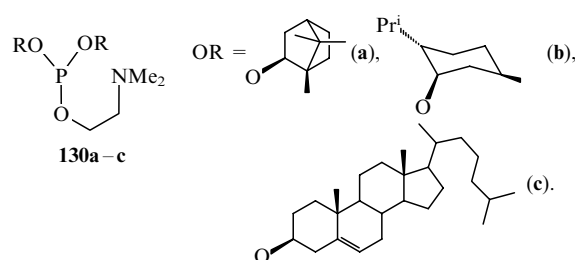
$n = m = 2$ (**a**); $n = 3, m = 1$ (**b**).

However, the use of the chiral P,N-bidentate derivatives of phosphorous acid **124** and **125a,b** in the hydrosilylation of acetophenone with diphenylsilane $\{[\text{Rh}(\text{CO})_2\text{Cl}]_2$ and $[\text{Rh}(\text{COD})\text{Cl}]_2$ as pre-catalysts $\}$ was not very effective (*ee* did not exceed 8%).¹⁵⁹

Ligand **129** was prepared¹⁶¹ by successive phosphorylation of diisopropyl tartrate and 4-aminomorpholine. It is coordinated as a P-monodentate ligand in the complex (acac)Rh(CO)L.



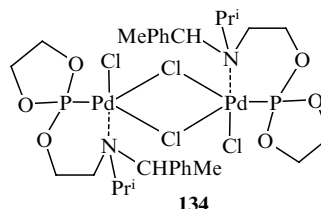
The complexes of phosphites **130–132** and phosphorous amide **133** with $\text{Pd}(\text{COD})\text{Cl}_2$ were studied by ^1H , ^{31}P and ^{13}C NMR, X-ray electron and IR spectroscopy and plasma desorption mass spectrometry.



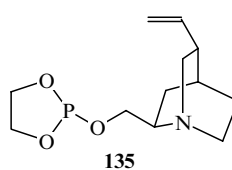
It was shown that the compounds **130a–c**^{162–164} and **133**¹⁶⁵ form mononuclear chelates of the same type. According to X-ray diffraction data, the Pd–P distance in the palladium complex of the ligand **130a** (2.189 Å) is shorter than this bond in palladium dichloro complexes with P,N-bidentate ligands forming a six-membered metallacycle (2.205–2.241 Å).¹⁶² The bond shortening is due to the π -acceptor properties of the phosphite centre.

The resonance signals of phosphorus in the ^{31}P NMR spectra of Pd(II) *cis*-dichloro complexes with amino phosphites and amino phosphorous amides occur at a higher field than the signals of free ligands due to shielding of the phosphorus nucleus. However, in the case of similar aminophosphine complexes, the signals of the ^{31}P nuclei are located at a lower field than those for the free ligands.¹⁶⁶

Dioxazaphosphocane **131** forms a polynuclear compound of Pd(II), namely, *cis*- $[\text{PdCl}_2(\text{L})]_{20}$, in which the P,N-bidentate ligands function as bridges arranged in the 'head-to-tail' manner.¹⁶⁷ From the 1,3,2-dioxaphospholane derivative **132**, the dimeric complex **134** with bridging chloro ligands and an intramolecular palladium–nitrogen bond was synthesised.¹⁶⁸ This unusual pattern of complexation observed for the ligand **132** is due to the presence of the bulky substituent in the peripheral amino group of its molecule. As a consequence, the amino group becomes a very weak nucleophile, an analogue of Hünig bases.



Recently,¹⁶⁹ aminoalkyl phosphite **135** based on a unique amino alcohol, quincoridin, has been synthesised.

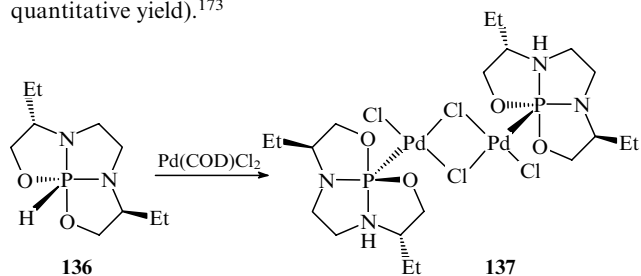


To the best of our knowledge, the compound **135** is the only known example of a P,N-bidentate ligand with a configurationally stable chiral nitrogen. This ligand was used to synthesise rhodium(I) chloro carbonyl chelate, $[\text{Rh}(\text{CO})\text{Cl}(\text{L})]$.

It should be noted that the increased (even in comparison with the most electron-withdrawing amino phosphites^{31,160}) π -acidity of the aminoalkyl phosphites **124**, **125a,b** and **135** influences the spectral characteristics of chloro carbonyl complexes of rhodium with these ligands. Thus the $^1J_{\text{P-Pb}}$ spin–spin coupling constants observed for these complexes are, on the average, ~ 100 Hz greater, while $\nu(\text{CO})$ values are greater by ~ 20 cm^{-1} .

Hydrophosphorane compounds are seldom used for the preparation of metal complexes with P,N-bidentate derivatives of phosphorous acid. Complex formation is accompanied by rupture of the P–H and P–N bonds and simultaneous formation of M–P and M–N bonds. The main studies dealing with the complexation of chiral hydrophosphoranes have been

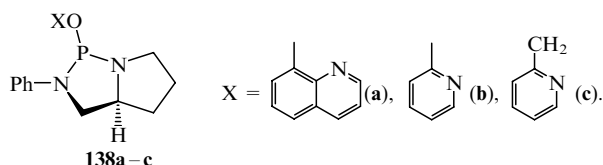
surveyed in several publications.^{155, 170, 171} Therefore, here we shall consider only the tricyclic hydrophosphorane **136**, prepared not long ago.¹⁷² The reaction of this compound with $\text{Pd}(\text{COD})\text{Cl}_2$ gave the first stable palladated phosphorane **137** (in an almost quantitative yield).¹⁷³



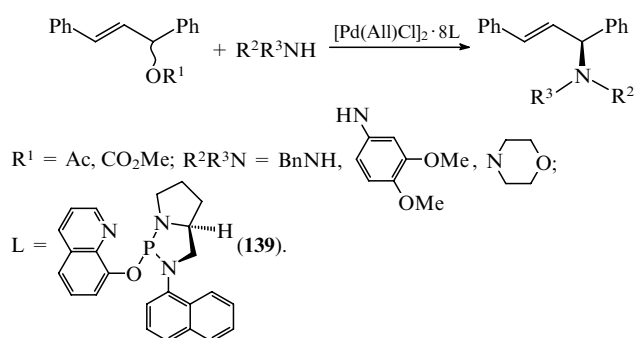
After the proton has migrated from phosphorus to nitrogen, the compound **136** acts as a P-monodentate phosphorane ligand. When **136** is made to react with $\text{Pt}(\text{COD})\text{Cl}_2$, the phosphorane ring is opened at the apical P–N bond. In the complex $[\text{PtCl}_2(\text{L})]$, the ligand occurs in the ‘open’ form and is bound to the metal in the P,N-bidentate fashion.¹⁷⁴

The synthesis and coordination to metals of phosphite and phosphorous amide derivatives of alkaloids, quinine and codeine, have been the subject of a detailed review;¹⁷⁵ therefore, we do not discuss them here.

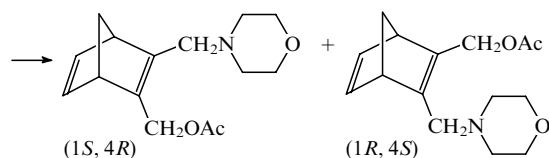
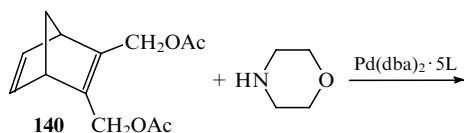
In 1997, diastereospecific synthesis of three amino-substituted phosphorous diamide ligands **138a–c** was reported.¹⁷⁶



In the classical allylic alkylation with the allyl acetate **12** {with $[\text{Pd}(\text{All})\text{Cl}]_2$ as the pre-catalyst}, the ligands **138a,b** ensured a degree of conversion of 100% and *ee* of 85%–87%, and the ligand **138c** provided 85% and 76%, respectively. Nearly identical results were attained in the related alkylation of dimethyl malonate with 3-methoxycarbonyloxy-1,3-diphenylprop-1-ene. Subsequently,¹⁷⁷ ligand **139** has been synthesised. The compounds **138a–c** and **139** (yields 70%–100%, *ee* 73%–94%) have found application as catalysts of allylic amination.



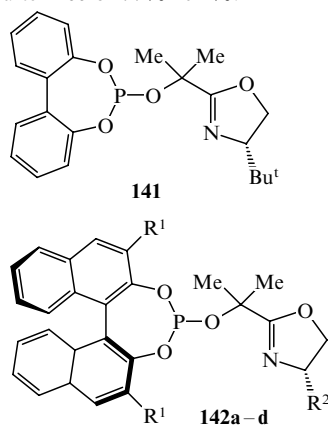
When diphenylallyl acetate is used as the substrate and benzylamine is employed as the nucleophile, the ligands **138a** and **138c** are the most effective (degree of conversion 95% and *ee* 93%). In the allylic amination of acetate **140** in the presence of the ligand **138a**, the yield is 93% and the optical yield is 89%.¹⁷⁸



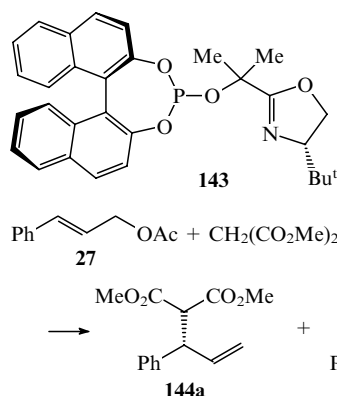
L = **138a**.

It is worth noting that known bisphosphines, (+)-DIOP and (–)-BINAP, ensure *ee* < 5% in this reaction.¹⁷⁸

4,5-Dihydrooxazoles **141–143**, containing cyclic phosphite groups as substituents, are effective ligands for catalytic allylation.^{179, 180} Thus alkylation of dimethyl malonate with the allyl acetate **27** in the presence of the $[\text{Pd}(\text{All})\text{Cl}]_2 \cdot 2.5\text{L}$ catalytic system results in *ee* of 77%–92%.



$\text{R}^1 = \text{H}$; $\text{R}^2 = \text{Bu}^t$ (**a**), Pr^i (**b**), Ph (**c**); $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Bu}^t$ (**d**).



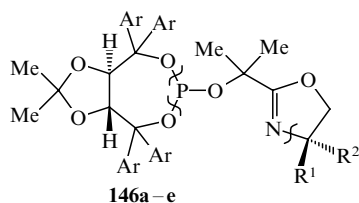
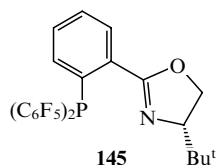
The best result was achieved in the presence of the ligand **142d**, the total yield of branched (**144a**) and linear (**144b**) reaction products being equal to 75%–92%.

Asymmetric induction is mainly accomplished due to the dihydrooxazole fragment. Thus for the ligand **141**, the *ee* is 83% and for the ligand **143**, it is 79%. In addition, the enantio- and regioselectivity of the process increase with an increase in the size and, especially, electronegativity of substituents at the phosphorus atom. The results of alkylation of dimethyl malonate with the acetates **27a,b** are listed in Table 2. It can be seen that both an increase in the size of substituents in the ligand and an increase in

Table 2. Enantio- and regioselectivity of the alkylation of dimethyl malonate with the acetates **27** $\{[\text{Pd}(\text{All})\text{Cl}]_2$ as the pre-catalyst}.

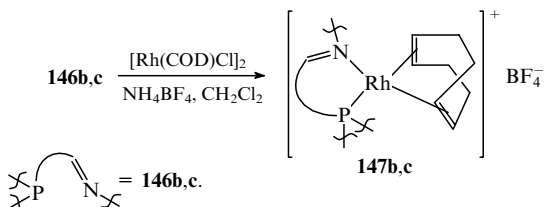
Compound 27	Ligand	<i>ee</i> (%)	The ratio 144a : 144b
a	23c	78	4 : 96
	145	84	47 : 53
	142a	90	76 : 24
	142a	96	95 : 5
b	142a	96	95 : 5

the steric requirements in the compound **27** results in higher enantioselectivity and regioselectivity of the reaction. It should be noted that the selectivity increases also on passing from the ligand **23c** to its analogue **145**, having perfluorophenyl groups attached to phosphorus.



Compound 146	Ar	R ¹	R ²
a	Ph	H	Ph
b	Ph	Ph	H
c	Ph	H	Pr ⁱ
d	Ph	Pr ⁱ	H
e	2-naphthyl	Pr ⁱ	H

Ligands **146a-e**, prepared using widespread chiral inducers, $\alpha,\alpha,\alpha',\alpha'$ -tetraaryl-1,2-dioxolano-4,5-dimethanols (TADDOL), were employed¹⁸¹ to prepare Rh(I) cationic complexes **147b,c** (the complex **147b** was characterised by X-ray diffraction analysis) and to carry out hydrosilylation of a series of aliphatic and aromatic ketones, including reduction of acetophenone with diphenylsilane {with [Rh(COD)Cl]₂ as the pre-catalyst}.



The best results were obtained with the ligand **146d**: the *ee* value in the reduction of acetophenone was 88% (chemical yield 91%) and in the reduction of *tert*-butyl methyl ketone, the *ee* reached 95%.

V. Conclusion

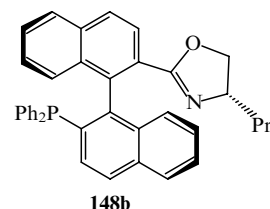
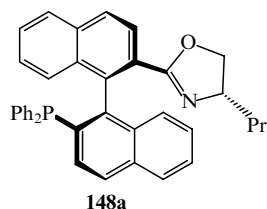
The data considered here demonstrate that the research into chiral P,N-bidentate ligands is developing rather vigorously. More than 270 compounds of this type are being used in asymmetric catalysis for allylic alkylation, cross-coupling, hydrosilylation of the C=O and C=C bonds, hydroboration-oxidation, hydroboration-amination and for the Heck reaction.

The use of rhodium and palladium complexes with optically active P,N-bidentate ligands in asymmetric catalysis is briefly summarised in Table 3. The table presents the results of the most thoroughly developed processes, namely, hydrosilylation, hydroboration-oxidation and allylic substitution. The enantioselective allylation was considered taking the model allylic alkylation of dimethyl malonate with the acetate **12** as an example. It follows from the data of Table 3 that phosphorus-substituted ferrocenes and dihydrooxazoles are the most effective in the hydrosilylation of the C=O bond; ferrocenylphosphinopyrazoles and QUINAP **103** are the best compounds for hydroboration-oxidation; and all the groups of chiral P,N-bidentate compounds proved efficient for

allylic substitution. It should also be noted that ferrocenylaminoalkylphosphines are effective stereoselective ligands for some cross-coupling reactions.

However, several topical problems in the chemistry of P,N-bidentate ligands are still to be solved.

(i) Among the problems of design and synthesis of these ligands, preparation of compounds with a chiral carbon atom at the phosphorus centre deserves attention in the first place because at present, predominant structures are those having asymmetric carbon atoms at the nitrogen centre and/or in the bridge linking phosphorus and nitrogen. It is also important to synthesise ligands with asymmetric donor atoms, especially, with configurationally stable chiral nitrogen atoms. Combination in a chiral ligand molecule of asymmetric atoms with different absolute configurations and chemical natures as well as combination of different types of chirality (for example, central and planar chirality, central and axial chirality, *etc.*) can provide effective transfer of chiral information from the metal complex to the substrate. For example, recently, phosphinodihydrooxazoles **148a,b** with a chirality axis were synthesised;^{182,183} allylic amination of the acetate **27** with substituted hydrazines¹⁸³ in the presence of these compounds results in *ee* of up to 99%, while the allylic alkylation of the allyl acetate **12**¹⁸² gives *ee* of up to 91%. It was shown¹⁸² that the binaphthalene cage is responsible for the increase in the stereoselectivity.



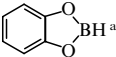
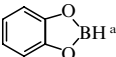
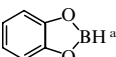
As noted above, an increase in the π -acidity of the phosphorus centre favours an increase in the chemical and optical yields in allylic substitution, hydroboration-oxidation and hydrosilylation of alkenes and hydrosilylation of ketones. The inductive effect of the phosphorus centre increases on passing from aminophosphines to amino phosphites or amino phosphorous amides. In these compounds, the inductive effect can be readily optimised.

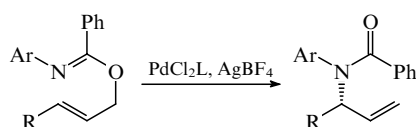
In the development of new chiral P,N-bidentate ligands, optically active natural products can be used such as steroids, amino acids and alkaloids. No P,N-bidentate derivatives of phosphorous acid having a plane of chirality or a peripheral imino group are known to date. However, the synthesis of these compounds is quite practicable.

It should also be noted that the synthesis of phosphites and phosphorous amides involves phosphorylation of the corresponding proton-donating functional groups, which proceeds, as a rule, with high yields; therefore, one can expect that a new generation of P,N-bidentate ligands would contain a phosphite (or amino phosphite) centre, possess planar or axial chirality of the carbon framework, and the nitrogen-containing fragment would be represented by an oxazoline, oxazine, imine or pyrazoline group.

(ii) Regarding asymmetric catalysis, it is necessary to master those reactions in which optically active P,N-bidentate ligands have received little use, if any. This refers first of all to the addition of electrophilic reagents to alkenes (for example, hydrocyanation) and to hydroformylation and copolymerisation of alkenes or dienes in the presence of CO. Non-symmetrical phosphinophosphites,¹⁵⁶ *i.e.* systems with donor centres with different chemical natures, showed good results in these reactions. An example of using P,N-bidentate ligands in non-standard reactions is the aza Claisen rearrangement catalysed by the complexes PdCl₂L [L = (*S,S*)-**11b**, **26b,c,f**].¹⁸⁴

Table 3. Comparative efficiency of some P,N-bidentate ligands in model catalytic reactions.

Substrate	Reagent	Pre-catalyst	Ligand	Reaction product	Yield (%) [<i>ee</i> (%)]	Ref.
PhCOMe	Ph ₂ SiH ₂	[Rh(COD)Cl] ₂	(<i>S,S,S</i>)-DIPOF (16)	PhCH(OH)Me	100 (91)	45
	Ph ₂ SiH ₂	[Rh(NBD)Cl] ₂	(<i>S,R</i>)- 176	PhCH(OH)Me	90 (90)	46
	Ph ₂ SiH ₂	[Rh(COD)Cl] ₂	26r	PhCH(OH)Me	99 (86)	90
	Ph ₂ SiH ₂	[Rh(COD)Cl] ₂	39	PhCH(OH)Me	84 (94)	91
	Ph ₂ SiH ₂	[Rh(COD)Cl] ₂	146d	PhCH(OH)Me	91 (88)	181
PhCH=CH ₂		[Rh(COD) ₂] ⁺ BF ₄ [−]	6g	PhCH(OH)Me	68 (98.5)	31
		[Rh(COD) ₂] ⁺ BF ₄ [−]	8b	PhCH(OH)Me	100 (87)	87
		[Rh(COD) ₂] ⁺ SO ₃ CF ₃ [−]	QUINAP (103)	PhCH(OH)Me	71 (91)	138
CH ₂ (CO ₂ Me) ₂	PhCH=CHCH(OAc)Ph	[Pd(All)Cl] ₂	(<i>S,S</i>)- 11b	PhCH=CHCH(Ph)CH(CO ₂ Me) ₂	98 (99)	43
	PhCH=CHCH(OAc)Ph	[Pd(All)Cl] ₂	26b,c,e	PhCH=CHCH(Ph)CH(CO ₂ Me) ₂	99 (99)	51–53, 56
	PhCH=CHCH(OAc)Ph	[Pd(All)Cl] ₂	40	PhCH=CHCH(Ph)CH(CO ₂ Me) ₂	94 (98)	82
	PhCH=CHCH(OAc)Ph	[Pd(All)Cl] ₂	41	PhCH=CHCH(Ph)CH(CO ₂ Me) ₂	99 (95)	83
	PhCH=CHCH(OAc)Ph	[Pd(All)Cl] ₂	43n	PhCH=CHCH(Ph)CH(CO ₂ Me) ₂	78 (98)	86
	PhCH=CHCH(OAc)Ph	[Pd(All)Cl] ₂	75h	PhCH=CHCH(Ph)CH(CO ₂ Me) ₂	70 (76)	112
	PhCH=CHCH(OAc)Ph	[Pd(All)Cl] ₂	76b	PhCH=CHCH(Ph)CH(CO ₂ Me) ₂	96 (96)	113
	PhCH=CHCH(OAc)Ph	[Pd(All)Cl] ₂	98	PhCH=CHCH(Ph)CH(CO ₂ Me) ₂	82 (86)	113
	PhCH=CHCH(OAc)Ph	[Pd(All)Cl] ₂	QUINAP (103)	PhCH=CHCH(Ph)CH(CO ₂ Me) ₂	94 (98)	140
	PhCH=CHCH(OAc)Ph	[Pd(All)Cl] ₂	121	PhCH=CHCH(Ph)CH(CO ₂ Me) ₂	85 (92)	151
	PhCH=CHCH(OAc)Ph	[Pd(All)Cl] ₂	138b	PhCH=CHCH(Ph)CH(CO ₂ Me) ₂	100 (87)	176
	PhCH=CHCH(OAc)Ph	[Pd(All)Cl] ₂	148b	PhCH=CHCH(Ph)CH(CO ₂ Me) ₂	99 (91)	182

^a Followed by treatment with H₂O₂ and NaOH.

The use of phosphinodihydrooxazoles as ligands in cross-coupling, hydroboration and hydrosilylation of alkenes appears quite promising. It is necessary to study already known amino phosphites, amino phosphorous amides and phosphitodihydrooxazoles not only in allylic substitution reactions but also in all other catalytic processes in which ligands with electron-withdrawing P-donor centres can participate. These studies would substantially extend the scope of application of chiral P,N-bidentate ligands in enantioselective catalysis. Further perfection of well-developed processes is needed, first of all, in order to achieve quantitative enantioselectivity (for example,¹⁸⁵ it is known that certification of pharmaceutical preparations requires *ee* ≥ 99%). The enantioselectivity can be increased by introducing non-chiral additives.¹⁸⁵

(iii) Investigation into the mechanisms of catalytic reactions can provide the basis for recommendations on the reaction conditions and for targeted synthesis of optimal ligands. Despite the impressive progress in modern asymmetric catalysis, it largely relies on the rules obtained empirically. This is partly due to the necessity of taking into account too many factors influencing the outcome of a catalytic reaction such as the nature of the ligand and the metal, the ligand:metal and catalyst:substrate ratios, the temperature, the concentration, the nature of the solvent, the additives present, *etc.* and, to some extent, this is due to the absence of a detailed investigation of the mechanisms of catalytic reactions.

(iv) In the field of coordination chemistry, it appears topical to continue the studies on the regularities of complexation of the main groups of ligands. Unfortunately, isolation and reliable characterisation of complexes with transition metals is far from being performed for all the P,N-bidentate ligands effective in catalysis.

Thus, despite the considerable contribution of iminophosphine derivatives, such as the ligands **118a–g** or **123a–f**, to asymmetric catalysis, the coordination behaviour of these ligands has scarcely been studied. This also concerns several other effective stereoselective ligands, **138**, **139** and **141–145**. The complex formation of related compounds **124**, **125**, **129** and **130–135** has been extensively studied; however, no data on the use of these compounds in catalytic processes can be found. Evidently, catalytic experiment and the study of the structures of pre-catalysts and related metal complexes for each group of ligands should be combined with investigation of the coordination and catalysis mechanism.

It appears useful to synthesise a series of related complexes with different ligands (as has been done, for example, for chloro carbonyl rhodium derivatives of phosphinoferrrocenylpyrazoles **6a–t**³¹). Comparison of the characteristic features of coordination of these compounds to metals and their spectroscopic properties and estimation of the electronic effects of the electron-donating centres would permit more efficient prediction of catalytic experiments and elucidation of the corresponding correlations. This integrated approach has been realised to some extent for ferrocenylaminophosphines (including PPFA **1** and PTFA **3**), phosphinoferrrocenylpyrazoles and phosphinodihydrooxazoles. However, even for these compounds, further studies are needed because P,N-bidentate coordination and chelation cannot be postulated *a priori* even for well-known ligands (for example, in the ligand **80b**, P,C_σ- rather than P,N-binding predominates).

It is clear that the current state of asymmetric catalysis and the prospects for its development are determined by not only P,N-bidentate ligands. Considerable contribution is made by P,P-, P,O- and N,N-bidentate systems (see, for example, several studies^{4–10, 186}).

It can be stated with confidence that the use of P,N-bidentate compounds opens a new stage in the development of coordination chemistry and asymmetric catalysis.

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^b — *Russ. Chem. Bull. (Engl. Transl.)*

^a — *Russ. J. Coord. Chem. (Engl. Transl.)*

^a — *Russ. J. Inorg. Chem. (Engl. Transl.)*

Inter-ring haptotropic rearrangements in π -complexes of transition metals with polycyclic aromatic ligands

Yu F Oprunenko

Contents

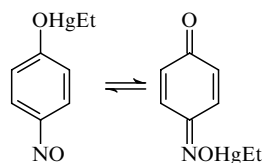
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Abstract. The results of studies of inter-ring haptotropic rearrangements in π -complexes of transition metals with polycyclic aromatic ligands are discussed. Syntheses and structures of model compounds are surveyed and the classification of dynamic processes in these compounds is proposed. The major regularities, mechanisms and kinetics of inter-ring haptotropic rearrangements in these systems are analysed. The bibliography includes 143 references.

I. Introduction

Diversified dynamic processes occur in molecules of different heteroorganic compounds (HOC) and, in particular, organometallic compounds (OMC), due to changes in the mutual arrangement of various groups in HOC molecules (rotation, small-amplitude oscillation, formation and cleavage of agostic bonds, inversion, etc.). Generally, these processes are degenerate and occur rather rapidly and hence, they are studied primarily by dynamic NMR spectroscopy.¹

One of the dynamic processes most commonly observed in HOC and OMC involves rapid migration of an element (metal) together with the ligand environment from one position in the organic fragment to another. For this type of tautomerism, Academician A N Nesmeyanov introduced the term 'metallotropic tautomerism' (metallotropy). He was the first² to find metallotropic rearrangements in nitrosophenyl and quinoxime compounds of mercury.

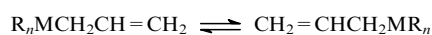


Hoffmann³ extended the term 'sigmatropic rearrangements' to π -complexes of transition metals and introduced the term 'haptotropic' rearrangements for these processes. Metallotropy is among the most important problems of chemistry because the

reactivities and catalytic activities of OMC are to a large extent determined by the tautomer ratio.⁴

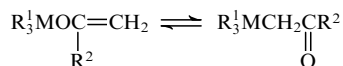
Metallotropic tautomerism has been studied for more than 40 years. A rich variety of metallotropic rearrangements have been thoroughly studied and a number of basic concepts have been offered, for example, the concepts of dual reactivity and σ, π -conjugation,⁵ stereochemically nonrigid organometallic compounds⁶ and catalytic and intramolecular activation of CH bonds,⁷ which made a noticeable impact on the development of the general theory of chemical bonds, catalytic activity and reactivity of OMC.

Degenerate σ, σ - and π, π -rearrangements in HOC and OMC were among the first to be discovered.^{8,9} For example, σ, σ -rearrangements in allylic complexes of magnesium,¹⁰ boron¹¹ and silicon¹² ([1,3]-sigmatropic rearrangements according to Woodward–Hoffmann) proceed through an intramolecular mechanism.¹³



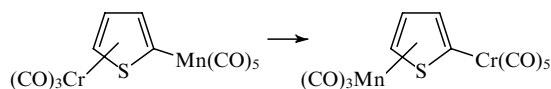
$n = 1, M = Mg; n = 2, M = B; n = 3, M = Si.$

Rearrangements of *C*- and *O*-substituted derivatives of carbonyl compounds containing MR_3 groups ($M = Ge$ or Sn)^{14,15} as well as the nitrosophenol–quinoxime rearrangement of mercury compounds described above (the first metallotropic rearrangement observed experimentally)² may also be assigned to this type of rearrangements.



$M = Ge, Sn.$

Migration of the organometallic group in the compounds described above is accompanied by rearrangement of the system of multiple bonds. Cross experiments demonstrated that these processes can occur both according to intramolecular and intermolecular mechanisms, but an intramolecular mechanism prevails. Formally, σ, σ -rearrangements are analogues of prototropic rearrangements in organic compounds, whereas σ, π - and π, π -rearrangements have no analogues because migrations of organometallic groups in the latter cases lead to a change in the character of a delocalised multicentre bond. For example, an interesting diotropic σ, π -rearrangement was observed in a binuclear thiophene complex.¹⁶

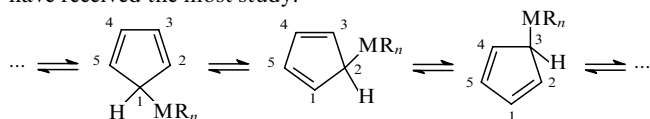


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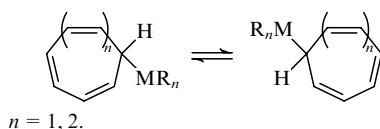
Uspekhi Khimii 69 (8) 744–766 (2000); translated by T N Safonova

The [1,5]-sigmatropic rearrangements in cyclopentadienyl and indenyl compounds of many main-group and transition metals have received the most study.¹⁷

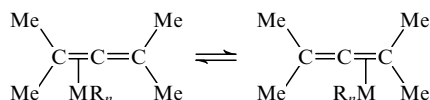


M = Si, Sn, Ge.

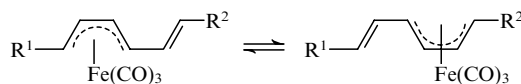
These rearrangements were also observed in cycloheptatrienyl¹⁸ and cyclononatetraenyl¹⁹ compounds.



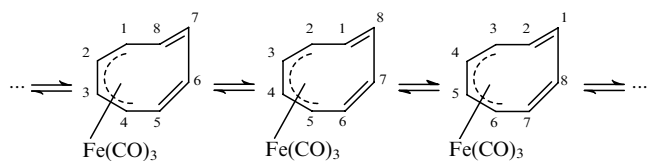
Generally, the activation barriers to these migrations are rather low and the migrations are degenerate in the sense that the molecule either undergoes internal conversion or is converted into a mirror image. Hence, these migrations are studied by dynamic NMR spectroscopy.²⁰ Molecules of this type can be described as 'stereochemically nonrigid' in terms proposed by Muettterties.²¹ Cotton²² introduced the term 'fluxional molecule' for their description. Haptotropic rearrangements in monocyclic π -complexes were considered in numerous reviews and monographs.^{23–25} For π -complexes of open polyenes, rearrangements of η^2 -allene²⁶ and η^4 -triene²⁷ derivatives have been studied most extensively.



$MR_n = Fe(CO)_4, Fe(CO)_2(\eta^5-C_5H_5).$

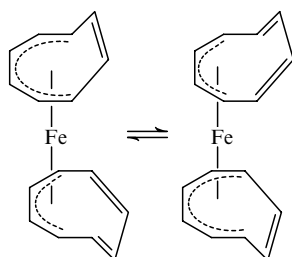


π, π -Rearrangements are often observed in π -complexes of open or cyclic conjugated polyenes with transition metals. These rearrangements are very diverse.²⁸ The η^4, η^4 -rearrangement of the tricarbonyliron complex of cyclooctatetraene provides a typical example. In the course of isomerisation, the $Fe(CO)_3$ group migrates along the system of the conjugated double bonds of the ligand.²⁹



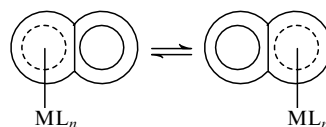
It should be noted that haptotropic rearrangements occur in π -complexes in which the π -ligand can be coordinated to the metal atom through several coordination sites and not all these sites are used, *i.e.*, some double bonds are not involved in coordination.

In $(\eta^4\text{-cyclooctatetraene})(\eta^6\text{-cyclooctatetraene})$ iron, migration of the metal atom is accompanied by a change in the mode of bonding in each ligand (*i.e.*, the η^4, η^6 -rearrangement).³⁰



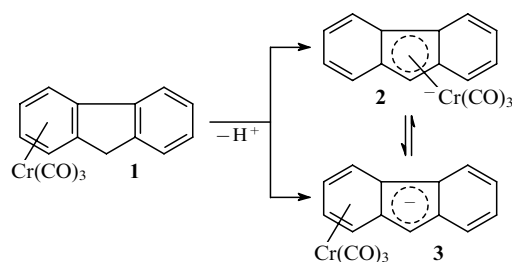
In early studies, metallotropy in OMC, including metallotropic rearrangements with the participation of the hydrogen atom and alkyl groups, was investigated primarily in open or monocyclic compounds.^{30–34} Much later, inter-ring rearrangements, rapid within the NMR time scale, were found, for example, in nickel complexes of naphthalene³⁵ and anthracene,³⁶ phenalenyl palladium complex³⁷ and dibenzenepentalenyl manganese complex.³⁸

Formally, π -complexes of transition metals (in particular, carbonyl chromium complexes, which are the most readily available and well-studied compounds) with polycyclic aromatic neutral ligands (naphthalene, acenaphthene, acenaphthylene, biphenylene, biphenyl, fluoranthene, *etc.*) are promising models for searching for and revealing new types of haptotropic rearrangements. In these systems, inter-ring haptotropic rearrangements (IHR) involving migration of the transition metal atom together with the ligand environment between the rings of the polyaromatic ligand can proceed.³⁹



Studies of the general regularities of IHR are of considerable importance because they can allow one to obtain further insight into the nature of the transition metal–ligand bond and to elucidate the mechanisms of catalytic processes occurring in solution under the action of metal-complex catalysts because IHR are involved as particular elementary stages in these processes.

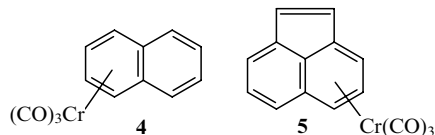
In 1971, Nicholas *et al.*⁴⁰ found for the first time nondegenerate IHR. Thus deprotonation of a solution of tricarbonyl(η^6 -fluorene)chromium (**1**) in DMSO with potassium *tert*-butoxide afforded tricarbonyl(η^5 -fluorenyl)chromium (**2**). The authors suggested that tricarbonyl(η^6 -fluorenyl)chromium (**3**) formed in the initial step of the reaction underwent a η^6, η^5 -rearrangement. The anion **3** was not detected by spectral methods and the kinetics and mechanism of its conversion into the isomeric η^5 -anion **2** were not studied in detail.



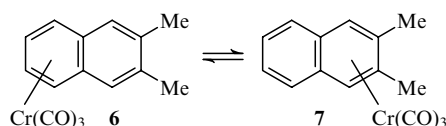
Later, inter-ring haptotropic rearrangement in the η^6 -anion **3** was studied in detail by Russian^{41–43} and Italian⁴⁴ researchers using IR and NMR spectroscopy and the kinetic and thermodynamic parameters of this rearrangement were determined. It was found that deprotonation of the complex **1** with a base gave rise to the η^6 -anion **3**, which was isomerised to form the η^5 -anion **2**. This rearrangement is reversible and entropy-controlled. The kinetic and thermodynamic parameters ($E_a = 16.29 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -19.62 \text{ e.u.}$) are to a large extent determined by the equilibrium between different ion pairs of the corresponding fluorenyl salts [contact ion pairs (CIP), separated ion pairs (SIP) and ionic associates]. More recently, analogous η^6, η^5 -rearrangements were found in complexes of a series of carbo- and heterocyclic analogues of fluorene.⁴⁵

Nondegenerate inter-ring migrations in fluorenyl complexes are fairly well studied by stationary kinetic methods. Inter-ring migrations in complexes of naphthalene and related unsubstituted polyaromatic systems are degenerate and cannot be studied by conventional procedures. The researchers hoped to find rapid

migrations of the $\text{Cr}(\text{CO})_3$ group between two equivalent rings in the simplest model complexes, *viz.*, tricarbonyl(η^6 -naphthalene)-chromium (**4**)^{40,46} and related (η^6 -acenaphthylene)tricarbonyl-chromium (**5**),⁴⁷ by NMR spectroscopy. Specimens were heated to rather high temperatures; however, no dynamic processes were observed in the spectra. Until the mid-1980s, procedures for the investigation of these degenerate processes were lacking.



As early as 1966, Deubzer, a coworker of the Nobelist Fischer, found⁴⁸ that isomeric tricarbonylchromium π -complexes of 2,3-dimethylnaphthalene **6** and **7** underwent reversible η^6, η^6 -IHR ($E_a \approx 30 \text{ kcal mol}^{-1}$) at 90–110 °C. Both complexes involved in the rearrangement have been isolated from the reaction mixture in pure form (by fractional recrystallisation) and identified for the first time.



However, these pioneering results were not published and remained unknown over 17 years until they were cited in Ref. 47.

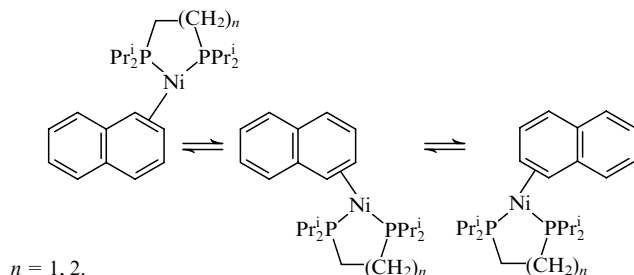
In succeeding years, inter-ring haptotropic rearrangements were studied by several research groups. Teams headed by P M Treichel (USA), E P Kündig (Switzerland), A Ceccon (Italy), Ch Elschenbroich (Germany), T A Albright (USA), M J McGlinchey (Canada), Yu A Ustynyuk and N A Ustynyuk (both from Russia) have made the major contribution to this line of investigation.

II. Classification and major regularities of inter-ring haptotropic rearrangements

The classification of IHR is as yet inadequate. I shall follow the classification of IHR depending on the type of bonding of the metal atom with the ligand proposed by N A Ustynyuk,⁴³ which is, in my opinion, the most reasonable and convenient one. According to this classification, the $3 \rightleftharpoons 2$ and $6 \rightleftharpoons 7$ rearrangements are assigned to η^6, η^5 - and η^6, η^6 -IHR, respectively.

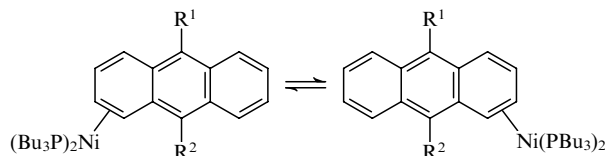
1. η^2, η^2 -Rearrangements in nickel complexes of naphthalene and anthracene

Recently, this type of rapid reversible degenerate rearrangement has been observed in phosphine complexes of nickel(0) with naphthalene³⁵ and anthracene.³⁶ The reactions of $[\text{Pr}_2\text{P}(\text{CH}_2)_n\text{PPr}_2]_2\text{Ni}$ ($n = 2$ or 3) with naphthalene^{49,50} in THF afforded complexes, which have η^2 -structures [according to the solid-state ^{13}C NMR spectra measured with the use of cross-polarisation and the magic-angle-spinning technique (CP MAS NMR)]. Solid-state and solution-phase two-dimensional exchange ^{13}C NMR spectra measured with magnetisation transfer demonstrated that the organonickel group migrates between double bonds both within one six-membered ring (E_a are 6 and



23 kcal mol^{-1} in solution and in the solid state, respectively) and between the rings. The migration between the rings is observed only in solution ($E_a = 15 \text{ kcal mol}^{-1}$).

The reactions of $(\text{Bu}_3\text{P})_3\text{Ni}$ with 5-alkyl- and 5,10-dialkylanthracenes⁴⁹ in benzene gave rise to η^2 -complexes whose structures were established by CP MAS ^{13}C NMR spectroscopy.

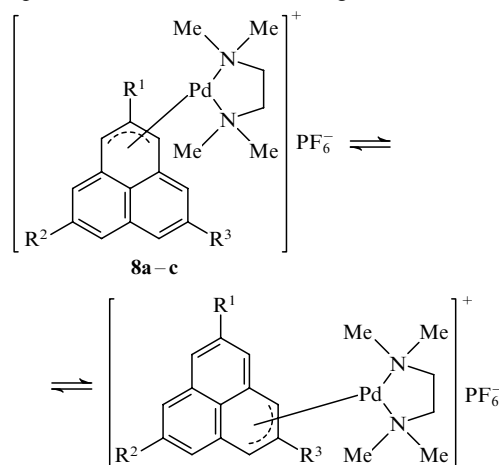


$\text{R}^1 = \text{Me, Et}; \text{R}^2 = \text{H, Me, Et}.$

Based on the data of ^1H and ^{13}C NMR spectroscopy, these complexes in solutions in benzene- d_6 underwent rapid η^2, η^2 -rearrangements, the organometallic group 'running around' the perimeter of the polycyclic ligand. The dynamic behaviour of these systems was studied using the spin saturation transfer technique and total line-shape analysis. In anthracene complexes, as in naphthalene complexes, the organonickel group was demonstrated to migrate within one ring and between the terminal rings both through intramolecular ($\Delta H^\ddagger = 8 \text{ kcal mol}^{-1}$) and intermolecular ($\Delta H^\ddagger = 20 \text{ kcal mol}^{-1}$) mechanisms.

2. η^3, η^3 -Rearrangements in phenalenyl complexes of palladium and rhodium

η^3, η^3 -Rearrangements were studied in most detail for η^3 -phenalenyl complexes. Thus the reactions of di- μ -chlorobis(η^3 -phenalenyl)dipalladium complexes dissolved in acetone with N, N, N', N' -tetramethylethylenediamine and KPF_6 afforded cationic palladium complexes of the allylic type **8a–c**.^{37,51} At 160 °C, coalescence of the signals for the aromatic protons was observed in the ^1H NMR spectrum of the complex **8a**, which is indicative of a dynamic process, *viz.*, a haptotropic shift of the organometallic group between the six-membered rings.³⁷

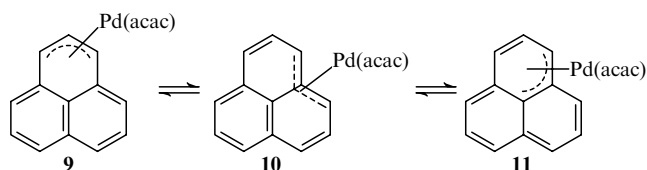


$\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$ (**a**); $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Me}$ (**b**);
 $\text{R}^1 = \text{Me}, \text{R}^2 = \text{R}^3 = \text{H}$ (**c**).

In the ^{13}C NMR spectrum of the compound **8b**, the signals for the allylic carbon atoms also coalesce at 102 °C. In this complex, the rate of the haptotropic rearrangement is higher and coalescence starts at lower temperature due apparently to the electronic effect of the methyl groups. The following activation parameters (at 90 °C) were determined from total line-shape analysis of the signals for the methyl groups in the spectra of the compounds **8b, c**.

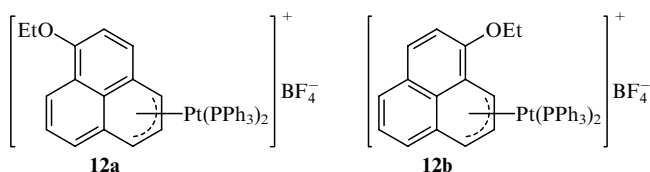
Compound 8	$\Delta H^\ddagger$ /kcal mol ⁻¹	$\Delta G^\ddagger$ /kcal mol ⁻¹	$\Delta S^\ddagger$ /e.u.	E_a /kcal mol ⁻¹
b	20.9 ± 0.4	21.4 ± 0.1	-1.3 ± 0.3	21.6 ± 0.4
c	23.1 ± 0.7	21.6 ± 0.1	4.1 ± 1.9	23.8 ± 0.7

The reaction of phenalene with Li_2PdCl_4 gave rise to the η^3 -phenalenyl palladium complex in 90% yield. Subsequent treatment of the latter with a solution of acetylacetone in benzene afforded η^3 -phenalenyl complex **9** in 50% yield.^{52,53} The possibility of η^3, η^3 -IHR occurring in the complex **9** was examined.

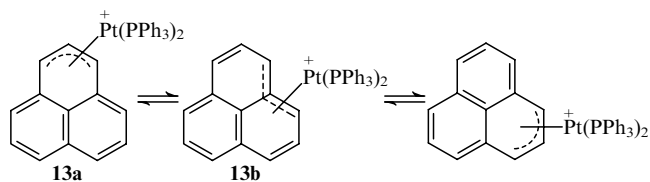


Calculations by the extended Hückel method demonstrated that structure **10** is less stable than structure **11** as the possible transition state. The difference between their energies is $1.21 \text{ kcal mol}^{-1}$. The energy of the structure **9** is $15.77 \text{ kcal mol}^{-1}$ lower than that of the structure **11**. Based on the results of calculations, it was concluded that the inter-ring haptotropic shift should occur through the transition state **10**. However, no dynamic processes were observed in the complex **9** by NMR spectroscopy, although η^3, η^3 -IHR would be expected to occur by analogy with the complexes **8**.

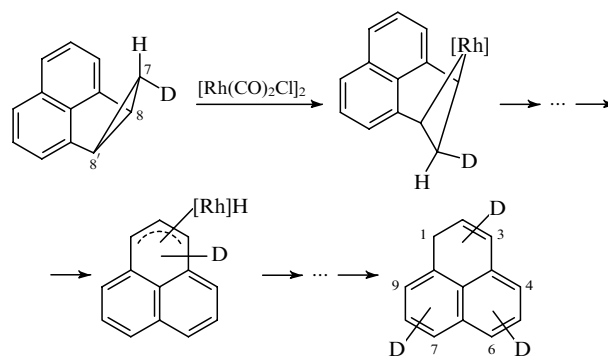
η^3 -Phenalenyl platinum complexes **12a, b** were prepared as yellow crystals by the reaction of 1-ethoxyphenalenium tetrafluoroborate with bis(triphenylphosphine)(η^3 -ethylene)platinum (the **12a** : **12b** ratio was 10 : 1).⁵⁴ The structures of the complexes **12a, b** were determined by ^{31}P NMR spectroscopy and X-ray diffraction analysis, but their dynamic behaviour in solution was not studied and the possibility of interconversion of the complexes **12a** and **12b** through inter-ring haptotropic rearrangements was not proved.



Calculations by the extended Hückel method demonstrated that the inter-ring haptotropic rearrangement in the η^3 -phenalenyl platinum complex **13a** should occur according to an intramolecular mechanism with a relatively low activation energy ($20.1 \text{ kcal mol}^{-1}$) through transition state **13b**.⁵⁵ The difference between the energies of the complexes **13a** and **13b** was found to be $3.83 \text{ kcal mol}^{-1}$.

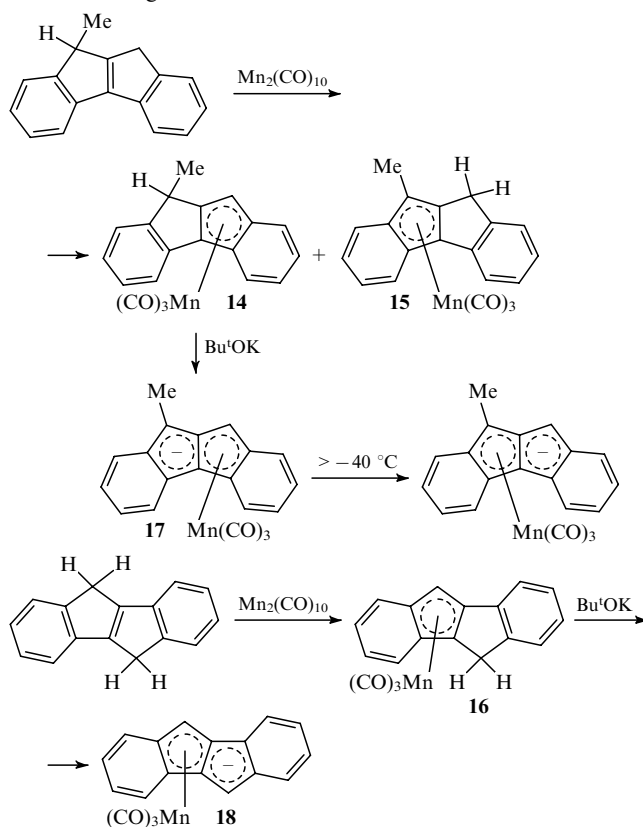


It was postulated that the η^3 -phenalenyl rhodium complex was formed in the reaction of the catalytic conversion of cycloprop[*a*]acenaphthylene into phenalene in the presence of the complex $[\text{Rh}(\text{CO})_2\text{Cl}]_2$.⁵⁶ The deuterium label introduced in the starting compound, for example, at position 7, is statistically distributed over positions 1, 3, 4, 6, 7 and 9 in the final product, *viz.*, in phenalene. This is attributable to the fact that the intermediate η^3 -phenalenyl rhodium complex undergoes η^3, η^3 -IHR involving migration of the metalohydride group between the six-membered rings with the 'ricochet' elimination of hydrogen.

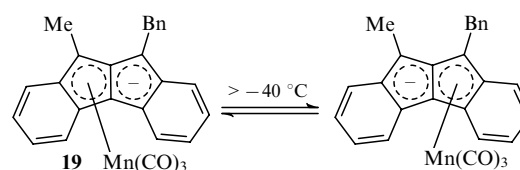


3. η^5, η^5 -Rearrangements in dibenzopentalenyl complexes of manganese

Only one example of η^5, η^5 -IHR is available in the literature. Refluxing of 9-methylindeno[1,2-*a*]indene or indeno[1,2-*a*]indene with $\text{Mn}_2(\text{CO})_{10}$ in dodecane for 1.5 h afforded isomeric dibenzopentalenyl complexes **14**–**16**, which differ in the type of fusion of the indene fragments.⁵⁷



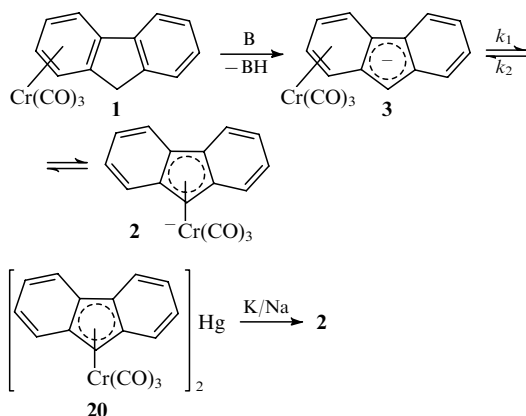
Deprotonation of the complexes **14** and **16** with potassium *tert*-butoxide gave rise to complexes **17** and **18**, respectively. In the compound **18**, no migration of the $\text{Mn}(\text{CO})_3$ group, rapid within the NMR time scale, was observed, whereas the complex **17** and the related benzyl complex **19** underwent rearrangements (in the case of the benzyl derivative, the rearrangement was reversible) to form the corresponding isomeric η^5 -complexes at temperatures above -40°C .



The difference in the behaviour of the complexes **17**–**19** was explained based on analysis of the node properties and energies of the highest occupied π -MO of the dibenzopentalenyl complexes **17** and **18** calculated by the INDO method.⁴³

4. η^6, η^5 -Rearrangements in fluorenyl complexes of chromium

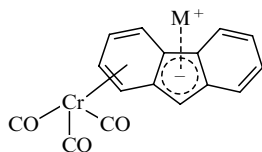
η^6, η^5 -Inter-ring haptotropic rearrangements have been studied comprehensively for indenyl and fluorenyl complexes of transition metals of the chromium and iron subgroups. For example, isomerisation in the anionic complexes of such ligands as indene, fluorene, their analogues containing different substituents in five- and six-membered rings and heterocyclic analogues of fluorene was considered in detail in reviews.^{41–43} In the present review, these data are briefly discussed and supplemented with new results. Thus tricarbonyl(η^6 -fluorene)chromium (**1**) is readily deprotonated with different bases, such as phosphoranes (for example, $\text{Ph}_3\text{P}=\text{CH}_2$), proton sponges, alkali metals in hexamethylphosphoramide (HMPA), BuLi and Bu⁺OM (M = Na, K, Rb or Cs),⁵⁸ in THF, ether, HMPA, dioxane and some other polar solvents. In these cases, the anion **3** is initially formed at rather low temperatures. At temperatures above -20°C , the η^6 -form **3** undergoes rapid rearrangement into the η^5 -form **2**. This accounts for the fact that Nicholas *et al.*⁴⁰ failed to detect the anion **3** at room temperature after deprotonation of the neutral complex **1**.



B is base.

The isomeric η^5 -anion **2** was also generated in the pure form by an independent synthesis involving reduction of symmetric mercury derivative **20** with a potassium–sodium alloy in ethereal solutions.

According to the data of IR spectroscopy, salts of the isomeric anions **2** and **3** exist in solution as equilibrium mixtures of contact ion pairs (CIP) and separated ion pairs (SIP) (Tables 1 and 2).^{59–62} In the IR spectra of these salts, the absorption bands in the region of ν_{CO} stretching vibrations of the $\text{Cr}(\text{CO})_3$ fragment are very characteristic, which allows one to obtain data on the type of ion pairs and to infer the position of the cation. In particular, no splitting of the E band of antisymmetric vibrations was observed in the IR spectrum of the contact ion pair formed by the anion **3**. Therefore, it can be concluded that the cation in this ion pair is located above the plane of the five-membered ring of the anion in the *trans* position with respect to the chromium atom.



In the contact ion pair formed by the anion **3**, the negative charge in the ring is substantially decreased due to the strong Coulomb cation–anion interaction. As a result, the symmetry C_{3v} of the $\text{Cr}(\text{CO})_3$ fragment is retained and the E band is degenerate (see Table 1). On the contrary, splitting of the E band is

Table 1. IR spectra of salts of the η^6 -anion **3** (ν_{CO}).

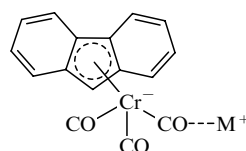
Cation	Solvent	Solvating additive	ν_A / cm^{-1}	ν_E / cm^{-1}	Type of ion pair
Li^+	THF	—	1927	1820, 1839	SIP
	HMPA	—	1928	1820, 1844	SIP
Na^+	THF	—	1925	1812, 1835	SIP
	HMPA	—	1928	1820, 1844	SIP
K^+	THF	DCH-18-C-6	1925	1821, 1840	SIP
	THF	—	1927	1817, 1841	SIP
	HMPA	—	1928	1820, 1844	SIP
Rb^+	THF	[2.2.2]-cryptand	1905	1822, 1842	SIP
	THF	—	1930	1840	CIP
	HMPA	—	1928	1819, 1843	SIP
Cs^+	THF	[2.2.2]-cryptand	1927	1820, 1844	SIP
	THF	—	1929	1840	CIP
	HMPA	—	1927	1821, 1843	SIP
Bu_4N^+	THF	[2.2.2]-cryptand	1928	1821, 1843	SIP
	THF	—	1924	1829	CIP
$\text{Ph}_3\text{P}^+\text{Me}$	THF	—	1927	1832	CIP
	HMPA	DCH-18-C-6	1927	1820, 1842	SIP

Note. DCH-18-K-6 is dicyclohexyl-18-crown-6.

Table 2. IR spectra of salts of the η^5 -anion **2** (ν_{CO}).

Cation	Solvent	Solvating additive	ν_A / cm^{-1}	ν_E / cm^{-1}	Type of ion pair
Li^+	THF	—	1915	1733, 1820	CIP
	HMPA	—	1904	1799	SIP
Na^+	THF	—	1907	1762, 1811	CIP
	HMPA	—	1904	1798	SIP
K^+	THF	DCH-18-C-6	1903	1800	SIP
	THF	—	1905	1766, 1807	CIP
	HMPA	—	1904	1798	SIP
Rb^+	THF	[2.2.2]-cryptand	1905	1800	SIP
	THF	—	1904	1766, 1804	CIP
	HMPA	—	1904	1798	SIP
Cs^+	THF	[2.2.2]-cryptand	1905	1800	SIP
	THF	—	1904	1778, 1798	CIP
	HMPA	—	1904	1789	SIP
Bu_4N^+	THF	[2.2.2]-cryptand	1905	1800	SIP
	THF	—	1903	1778, 1798	CIP
	$\text{Ph}_3\text{P}^+\text{Me}$	THF	1905	1802	CIP

pronounced in the IR spectra of the contact ion pair formed by the anion **2**, the degree of splitting depending on the nature of the cation (see Table 2). Such splitting indicates that the counterion is coordinated to the oxygen atom of one of the CO groups.



The anions **2** and **3** and bulky cations characterised by high charge delocalisation, such as Rb^+ , Cs^+ , Bu_4N^+ and $\text{Ph}_3\text{P}^+\text{Me}$, form predominantly contact ion pairs.

The η^6, η^5 -inter-ring haptotropic rearrangement of the anion **3** into the anion **2** and the reverse rearrangement were studied by ^1H NMR^{44, 60, 63} and IR spectroscopy.^{59, 64} For these rearrangements, the equilibrium constants (K_{eq}) and the rate constants of the forward and back reactions (k_1 and k_2 , respectively) were determined (Tables 3 and 4). The K_{eq} values (see Table 3) indicate that the metallotropic η^6, η^5 -equilibrium studied for a wide range

Table 3. Equilibrium constants for η^6, η^5 -IHR of salts of anions **2** and **3**.

Cation	Solvent	Type of 3 $\rightleftharpoons$ 2 equilibrium	$K_{\text{eq}} = 2k_1/k_2$
Li ⁺	HMPA	SIP $\rightleftharpoons$ SIP	5.40
	THF	SIP $\rightleftharpoons$ SIP	see ^b
Na ⁺	HMPA	SIP $\rightleftharpoons$ SIP	5.00
	THF	SIP $\rightleftharpoons$ SIP	13.7
K ⁺	HMPA	SIP $\rightleftharpoons$ SIP	4.92
	THF	SIP $\rightleftharpoons$ SIP	14.3
Rb ⁺	THF ^a	SIP $\rightleftharpoons$ SIP	4.40
	THF	CIP $\rightleftharpoons$ CIP	5.0
Cs ⁺	THF ^a	SIP $\rightleftharpoons$ SIP	4.60
	THF	CIP $\rightleftharpoons$ CIP	1.40
Ph ₃ PMe ⁺	THF	CIP $\rightleftharpoons$ CIP	3.40

^a HMPA was used as the solvating additive. ^b The K_{eq} value was not determined because the lithium salt of the anion **3** in a solution in THF was unstable.

Table 4. Rate constants and equilibrium constants of the **3** $\rightleftharpoons$ **2** rearrangement.⁵⁹

T/K	$10^{-4}k_1/s^{-1}$	$10^{-4}k_2/s^{-1}$	$K_{\text{eq}} = 2k_1/k_2$ (see ^a)
THF			
273	1.11	0.2	11.1
280	1.22	0.21	11.62
288.5	4.0	0.63	12.7
298	8.9	1.28	13.9
301	17.1	2.4	14.3
THF with a DCH-18-C-6 additive			
273	0.62	0.4	3.1
285.5	2.75	1.12	4.91
298	18.5	6.86	5.4

^a The possibility of the **3** $\rightleftharpoons$ **2** rearrangement occurring in both directions was ignored in the study⁵⁹ and, hence, only the refined K_{eq} values for the doubly degenerate process are given.

of systems is very sensitive to the structure of the ion pairs. The thermodynamic data given below testify that these η^6, η^5 -IHR are entropy-controlled processes. It should be noted that many reactions involving ion pairs are entropy-controlled, which is attributed to the fact that several solvent molecules are coordinated about the cation (solvate coat) in separated ion pairs resulting in a substantial decrease in the entropy of this state.⁶² The activation parameters of the **3** $\rightleftharpoons$ **2** rearrangement in THF in the presence and in the absence of the solvating additive (DCH-18-C-6) are given below:

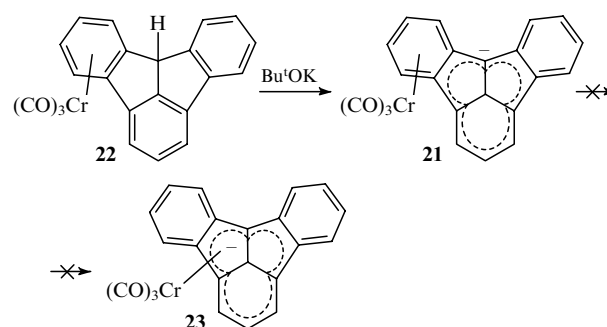
Solvent	E_a /kcal mol ⁻¹	$\Delta H^\ddagger$ /kcal mol ⁻¹	$\Delta S^\ddagger$ /e.u.
THF	16.3 $\pm$ 2.18	15.7 $\pm$ 2.04	-19.6 $\pm$ 2.55
THF + DCH-18-C-6	21.9 $\pm$ 2.13	21.3 $\pm$ 2.10	0.2 $\pm$ 0.02

Cross experiments demonstrated that at moderate temperatures η^6, η^5 -IHR in the anions **2** and **3** proceed through an intramolecular mechanism. In these processes, the tricarbonylchromium group is not eliminated and does not go into solution to form a complex with the solvent (for example, with THF).⁴¹

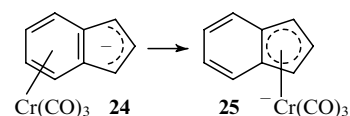
5. Rearrangements in anionic tricarbonylchromium η^6 - and η^5 -complexes of carbo- and heterocyclic analogues of fluorene

By going from the unsubstituted tricarbonylchromium complex of fluorene to its carbo- and heterocyclic analogues, one can sub-

stantially extend the range of systems in which η^6, η^5 -IHR occur and study the dependence of these processes on the electronic and steric effects of the substituents and heteroatoms.⁶⁵ The introduction of a heteroatom or a substituent into one of the rings of the π -ligand leads to a substantial change in the electron density in the latter. The isomer in which the organometallic group is bound to the ring possessing a higher electron density is thermodynamically more stable resulting in an increase in the content of this isomer in the equilibrium mixture. In the case of carbocyclic analogues of 9-substituted fluorenes (9-methyl-, 9-*tert*-butyl- and 9-phenyl-fluorenes), the ratio between the η^5 and η^6 -isomers depends on the electronic and steric effects of the substituent. The donor effect of the methyl group leads to an increase in the electron density in the five-membered ring of the fluorenyl anion and, correspondingly, to an increase in the proportion of the η^5 -isomer ($K_{\text{eq}} = [\eta^5]/[\eta^6] = 10$). On the contrary, the electron-withdrawing effect of the phenyl substituent leads to a decrease in the electron density in the five-membered ring and, correspondingly, to a decrease in the portion of the η^5 -isomer in the equilibrium mixture ($K_{\text{eq}} = [\eta^5]/[\eta^6] = 0.35$). Tricarbonyl(η^6 -fluoradenyl)chromium (**21**) formed upon deprotonation of fluoradene complex **22** does not undergo rearrangement to form the η^5 -anion **23**.⁶⁶ This is attributable to the fact that the negative charge is delocalised over two five-membered rings and the six-membered ring fused with these rings.

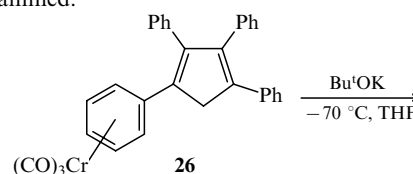


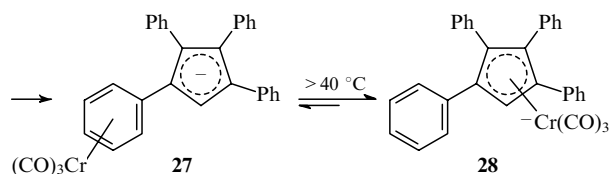
On the contrary, delocalisation of the negative charge in the five-membered ring in (η^6 -indenyl)tricarbonylchromium (**24**) is smaller than that in the fluorenyl analogue and hence, the anion of **24** is completely rearranged into the η^5 -isomer **25** in THF even at temperatures above -40 °C. The rate of the η^6, η^5 -inter-ring haptotropic **24** $\rightarrow$ **25** rearrangement is noticeably higher than that of the **3** $\rightarrow$ **2** rearrangement.



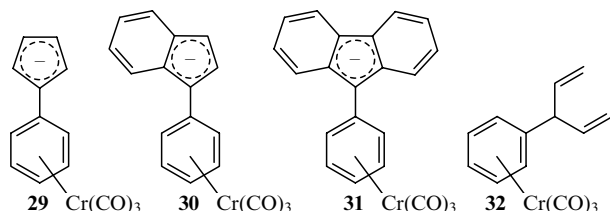
The phenyl substituent in the five-membered ring of the complex **24** (like that in the 9-phenylfluorenyl complex) decreases the electron density in the ring and hence, the equilibrium is shifted toward the η^6 -anion.⁴³

The Öfele reaction of tetraphenylcyclopentadiene with $\text{Py}_3\text{Cr}(\text{CO})_3$ afforded tricarbonyl[(η^6 -1-phenyl)-2,3,4-triphenylcyclopentadiene]chromium (**26**),⁶⁷ which is the nonannulated open analogue of (η^6 -indenyl)tricarbonylchromium. Deprotonation of the latter giving rise to the η^6 -anion **27** and the ability of the tricarbonylchromium group to migrate from the six-membered ring to the five-membered ring to form the η^5 -anion **28** were examined.





Ceccon *et al.* studied irreversible η^6, η^5 -IHR in the phenylcyclopentadienyl (**29**), 1-phenylindenyl (**30**) and 9-phenylfluorenyl (**31**) complexes of chromium⁶⁸ and the rearrangement in the very interesting open phenylpentadienyl system **32**.⁶⁹



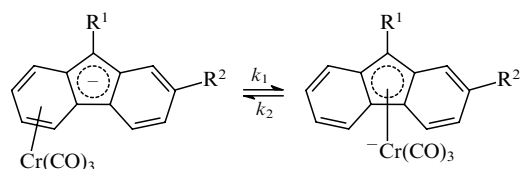
The activation parameters and the rate constants (k) of η^6, η^5 -IHR in the anions **29**–**31** are given below.

29: $\Delta S^\ddagger = -7.1 \pm 1.1$ e.u., $\Delta H^\ddagger = 22.7 \pm 0.4$ kcal mol⁻¹,
 T/K 325 332 337 342
 $10^4 k/s^{-1}$ 1.03 ± 0.03 2.32 ± 0.01 3.85 ± 0.02 6.21 ± 0.02

30: $\Delta S^\ddagger = -7.6 \pm 0.6$ e.u., $\Delta H^\ddagger = 22.3 \pm 0.4$ kcal mol⁻¹,
 T/K 324 325 341 346
 $10^4 k/s^{-1}$ 1.3 ± 0.02 4.32 ± 0.02 7.86 ± 0.03 12.5 ± 0.2

31: $\Delta S^\ddagger = 2.6 \pm 0.7$ e.u., $\Delta H^\ddagger = 24.3 \pm 0.02$ kcal mol⁻¹,
 T/K 338 343 348 353
 $10^4 k/s^{-1}$ 1.08 ± 0.01 1.84 ± 0.01 3.15 ± 0.06 5.20 ± 0.06

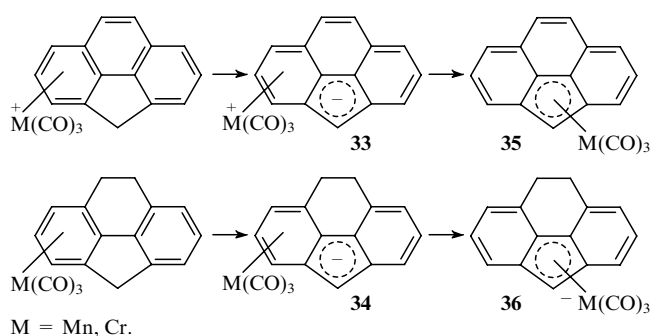
The kinetic parameters (298 K) of η^6, η^5 -IHR in 2-acetyl, 9-methyl- and 9-phenylfluorenyl complexes of chromium were determined.⁶⁴



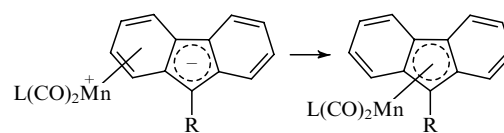
$R^1 = H, R^2 = COMe; R^1 = Me, R^2 = H; R^1 = Ph, R^2 = H.$

R^1	R^2	K_{eq}	$10^4 k_1/s^{-1}$	$10^4 k_2/s^{-1}$
H	H	6.37	4.0	0.63
Me	H	5.73	5.82	1.02
H	COMe	3.03	5.76	1.9

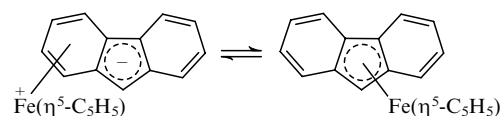
McGlinchey and coworkers studied⁷⁰ the rearrangements of the zwitterionic tricarbonylmanganese complexes and the anionic tricarbonylchromium complexes containing a very interesting ligand, *viz.*, 4H-cyclopenta(phenanthrene), or the corresponding hydrogenated ligand. The possible paths of these rearrangements and the transition states were investigated experimentally as well as theoretically by the extended Hückel method. The η^6, η^5 -inter-ring haptotropic rearrangements both in the manganese and chromium complexes **33** with the completely fused ligand proceed much more readily than those in the anions **34** prepared from the corresponding hydrogenated complexes. The η^6 -anions **33** are kinetically stable at temperatures below -40 °C. At higher temperatures, these anions undergo rearrangements into the η^5 -anions **35**, whereas the rearrangements of the hydrogenated anions **34** into anions **36** occur at high temperatures. The authors attributed this fact to the retention of the stable naphthalene system of the aromatic anion in the course of IHR.



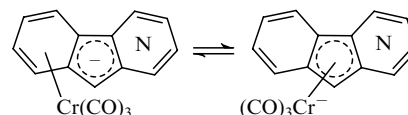
Relatively rapid η^6, η^5 -inter-ring rearrangements in the fluorenyl complexes of manganese,⁷¹ iron,⁷² molybdenum and tungsten⁷³ were studied. The E_a values of these processes were demonstrated to depend substantially on the nature of transition metal. The $\Delta H^\ddagger$ values are in the range of 24–25 kcal mol⁻¹ and the $\Delta S^\ddagger$ values vary from 2 to -1.6 e.u. The rearrangements in the manganese complexes are irreversible.⁷¹



$R = H, Bu^t; L = CO, PBu_3^t.$



Investigations of azafluorenyl systems by the INDO method demonstrated^{43, 74} that the introduction of the electronegative nitrogen atom into the six-membered ring leads to a decrease in electron density in the five-membered ring compared to that in the fluorenyl system, *i.e.*, the inter-ring haptotropic rearrangement results in a decrease in the portion of the η^5 -isomer.



The η^6, η^5 -inter-ring haptotropic rearrangements do not proceed in tricarbonylchromium complexes of carbazoyl and indolyl, which is difficult to explain within the framework of the above-described simplified approach because the electron density in the five-membered rings of these compounds is very high. Apparently, these rearrangements do not occur due to the fact that the electron pair at the nitrogen atom in the pyrrolyl, indolyl and carbazoyl anions occupies an MO orthogonal to the π -MO of the cyclic system, whereas the electron pair at the carbon atom in the cyclopentadienyl, indenyl and fluorenyl anions is involved in a π -MO participating in bonding with the metal atom.

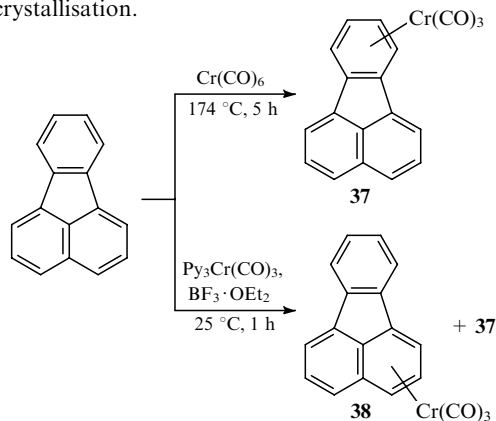
Experimental investigations of the structures and properties of isomeric η^6 - and η^5 -fluorenyl complexes and their analogues and examination of the mechanism of η^6, η^5 -IHR have been summarised.^{74–79} Analysis of the above-considered data demonstrates that the structure of the π -ligand, the nature of the metal atom and its ligand environment affect substantially the metal-ligand equilibrium, the site of location of the organometallic group depending to a large extent on the electron density in the five-membered ring. Apparently, the determination of enthalpies of isomeric complexes and transition states using high-level quantum-chemical calculations can improve the reliability of the prediction of the results of IHP.⁸⁰

6. η^6, η^6 -Rearrangements in tricarbonylchromium complexes of naphthalene and its analogues

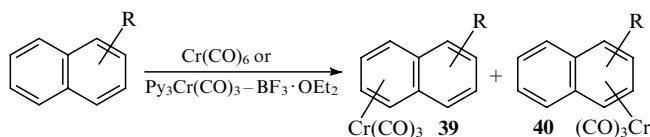
Deubzer⁴⁸ demonstrated that isomerisation of tricarbonylchromium complexes of 2,3-dimethylnaphthalene, which is the first example of η^6, η^6 -IHR available in the literature, proceeds slowly and is characterised by a high activation barrier. These results were indirectly confirmed in studies performed by Nicholas,⁴⁰ Kündig⁴⁶ and Albright⁴⁷ with their coworkers. The authors failed to detect the haptotropic rearrangement in tricarbonylchromium complexes of η^6 -naphthalene and η^6 -acenaphthylene by dynamic NMR spectroscopy upon heating of specimens in the probe of an NMR spectrometer. Analogously, inter-ring rearrangements, rapid within the NMR time scale, were not detected at relatively high temperatures in some other naphthalene complexes, for example, in $[(\eta^6\text{-C}_{10}\text{H}_8)\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)]^{2+}$ (70 °C, $\text{CF}_3\text{CO}_2\text{H}$)⁷⁷ and $(\eta^6\text{-C}_{10}\text{H}_8)_2\text{Cr}$ (130 °C, C_6D_6).⁴⁶

Hence, the only possible strategy for studying η^6, η^6 -rearrangements in π -complexes of naphthalene involves the removal of degeneration in these systems, *i.e.*, the use of unsymmetrically substituted compounds, and their study by stationary kinetics methods. This approach was developed in detail only in the mid-1980s.^{81–84} Initially, procedures have been proposed for the regioselective synthesis of tricarbonylchromium complexes of substituted naphthalenes containing a label at a particular position of the coordinated or uncoordinated ring of the naphthalene ligand.

Substituted naphthalenes can form tricarbonylchromium complexes upon heating with $\text{Cr}(\text{CO})_6$,⁸⁵ including reactions in the presence of polar additives⁸⁶ as catalysts. For example, boiling of $\text{Cr}(\text{CO})_6$ with naphthalene in decalin in the presence of ethyl formate afforded $(\eta^6\text{-C}_{10}\text{H}_8)\text{Cr}(\text{CO})_3$ in 88% yield.⁸⁷ Tricarbonylchromium complexes of substituted naphthalenes were also formed in the reactions of the ligand with $(\text{NH}_3)_3\text{Cr}(\text{CO})_3$ (the Rausch reaction⁸⁸) and with the $\text{Py}_3\text{Cr}(\text{CO})_3\text{-BF}_3\cdot\text{OEt}_2$ system (the Öfele reaction^{89,90}). Thus the reaction of fluoranthene with $\text{Cr}(\text{CO})_6$ performed under conditions of thermodynamic control gave rise to η^6 -complex **37** in which the $\text{Cr}(\text{CO})_3$ is located at the benzene ring.⁹¹ The synthesis with the use of the $\text{Py}_3\text{Cr}(\text{CO})_3\text{-BF}_3\cdot\text{OEt}_2$ system yielded complex **38** in which the $\text{Cr}(\text{CO})_3$ is located at the naphthalene fragment. The latter reaction also afforded a small admixture (< 5%) of the compound **37**, which was readily separated from the complex **38** by recrystallisation.



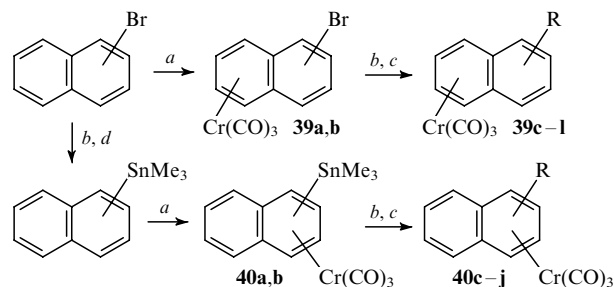
A convenient alternative procedure was developed for the synthesis of substituted naphthalenes. This procedure involves the migration of the tricarbonylchromium group from readily accessible $(\eta^6\text{-C}_{10}\text{H}_8)\text{Cr}(\text{CO})_3$ to another polyaromatic ligand.⁴⁶ The result of this complexation reaction depends on the conditions of control (either kinetic or thermodynamic), which can be used for preparative purposes. However, these methods for the synthesis of complexes of monosubstituted naphthalenes generally give rise to mixtures of both possible isomers **39** and **40** containing the tricarbonylchromium group either in the substituted or unsubstituted rings.



For alkyl-substituted complexes, the **39**:**40** ratio is close to unity and the isomers can be separated by chromatography (TLC or HPLC⁹²). It was demonstrated⁹³ that the very high regioselectivity of the Öfele reaction can be achieved if the substituent possesses pronounced electron-withdrawing or electron-donating properties. This behaviour agrees well with the results of calculations of the relative energies of isomeric tricarbonylchromium complexes of monosubstituted naphthalenes within the framework of density functional theory (DFT).⁸⁰

Thus under the conditions of the Öfele reaction, complexes of the type **39** are predominantly formed if $\text{R} = \text{Br}$, whereas complexes of the type **40** are obtained as the major products if $\text{R} = \text{SiMe}_3$ and, particularly, if $\text{R} = \text{SnMe}_3$. A thorough search for the reaction conditions enables one to achieve satisfactory yields (50% and higher).

The most general and versatile procedure for the regioselective synthesis of substituted complexes **39** and **40** involves the following reaction sequence. Initially, 1- and 2-bromo- or 1- and 2-trimethylstannyl naphthalenes are converted into the corresponding tricarbonylchromium complexes **39a,b** or **40a,b**, respectively, by the Öfele reaction.



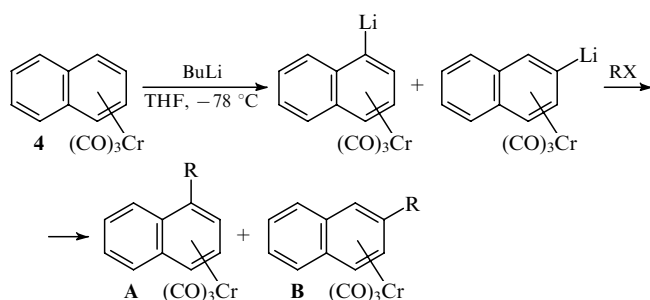
39: $\text{R} = 1\text{-Br}$ (**a**), 2-Br (**b**), 1-D (**c**), 2-D (**d**), 1-Me (**e**), 2-Me (**f**), 1-SiMe_3 (**g**), 2-SiMe_3 (**h**), 1-SnMe_3 (**i**), 2-SnMe_3 (**j**), 1-Cl (**k**), 2-Cl (**l**);

40: $\text{R} = 1\text{-SnMe}_3$ (**a**), 2-SnMe_3 (**b**), 1-D (**c**), 2-D (**d**), 1-Me (**e**), 2-Me (**f**), 1-SiMe_3 (**g**), 2-SiMe_3 (**h**), 1-Cl (**i**), 2-Cl (**j**);

(a) $\text{Py}_3\text{Cr}(\text{CO})_3\text{-Et}_2\text{O}\cdot\text{BF}_3$; (b) BuLi ; (c) RX ; (d) Me_3SnCl .

In the reactions of these complexes with BuLi in ether at -70 °C, the Br or SnMe_3 substituents are readily replaced by lithium. Under these conditions, the resulting organolithium compounds neither decompose nor undergo isomerisation. Subsequently, the latter compounds react with various electrophilic reagents to give the complexes **39c–l** or **40c–j** in yields varying from 50% ($\text{R} = \text{Cl}$) to 90% ($\text{R} = \text{D}$). It appeared that the reaction must be performed in ether because this reaction in THF is essentially complicated by intramolecular and intermolecular Li-H exchange (see below).⁹⁴

One of procedures for the selective introduction of a substituent into the coordinated ring involves direct metallation of tricarbonyl(η^6 -naphthalene)chromium (**4**) followed by treatment of the resulting organolithium compound with an electrophilic reagent.⁹³ It is known that coordination with the tricarbonylchromium group leads to a substantial increase in the acidity of the arene protons (the $\text{p}K_a$ values decrease by 6–7⁹⁵). The reaction with the use of BuLi as the metallating agent in THF at -78 °C proceeded nonselectively both at positions 1 and 2 of the coordinated ring to form mixtures of complexes following reactions with electrophiles.

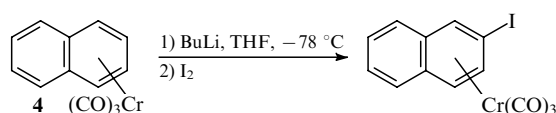


RX = D₂O, MeI, Me₃SiCl, Me₃SnCl.

If lithium salts are generated at a temperature below $-78\text{ }^{\circ}\text{C}$, the ratio between the isomers **A** and **B** in the mixture depends on the nature of the substituent.

RX	Total yield (%)	The ratio A : B
D ₂ O	87	0.80
MeI	66	0.56
Me ₃ SnCl	74	0.44
Me ₃ SiCl	45	0.31

The replacement proceeded regioselectively at position 2 (the yield was 20%) only in the reactions of lithium salts with I₂.



Kündig *et al.* demonstrated⁸³ that the use of sterically hindered 2,2,6,6-tetramethylpiperidyllithium instead of BuLi made it possible to perform regioselective metallation of tricarbonyl(η^6 -naphthalene)chromium. In this case, the replacement occurred exclusively at position 2, which may be due to steric hindrances to electrophilic attack at position 1.

III. Studies of mechanisms and kinetics of rearrangements in tricarbonylchromium complexes of polycyclic arenes

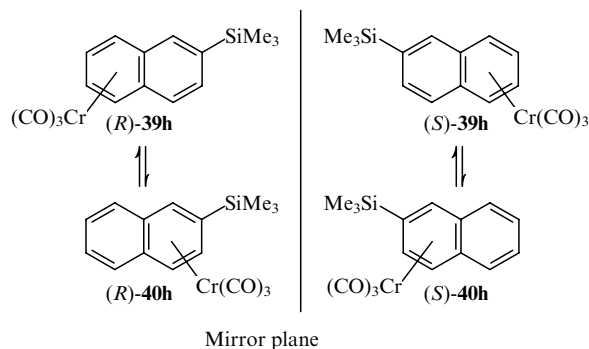
Elucidation of the mechanism is the vital problem in studies of chemical processes. For inter-ring haptotropic rearrangements in tricarbonylchromium complexes of polycyclic arenes, it is important to determine whether the reaction proceeds through an intramolecular or intermolecular dissociation mechanism. In the first case, the migration of the Cr(CO)₃ group along the ligand plane occurs without the cleavage of bonds with the ligand. In the second case, the Cr(CO)₃ group is eliminated from one ring of the ligand and passes into solution. Then this group is coordinated by solvent molecules containing a heteroatom followed by addition to another ring of the same ligand or to another ligand. Bimolecular reactions of the complexes can proceed as well (either with each other⁹⁶ or with free ligands formed upon thermal destruction of the complexes). The latter are accompanied by the migration of the tricarbonylchromium group in the ligand, *i.e.*, IHR can occur through an intermolecular exchange mechanism.

Previously, the intramolecular mechanism of η^6, η^5 -IHR in isomeric fluorenyl complexes **2** and **3** was confirmed by cross experiments.^{42,43} An analogous approach was used in studies of the mechanism of η^6, η^5 -IHR in tricarbonylchromium complexes of naphthalene derivatives. For this purpose, the redistribution of the tricarbonylchromium group between naphthalene and perdeuterionaphthalene was examined.⁹³ It was found that even prolonged heating ($90\text{ }^{\circ}\text{C}$, $>40\text{ h}$) of the complex **39e** with perdeuterionaphthalene in anhydrous decane did not lead to migration of the tricarbonylchromium group to perdeuterionaphthalene. Although the **39e** $\rightleftharpoons$ **40e** inter-ring haptotropic migration

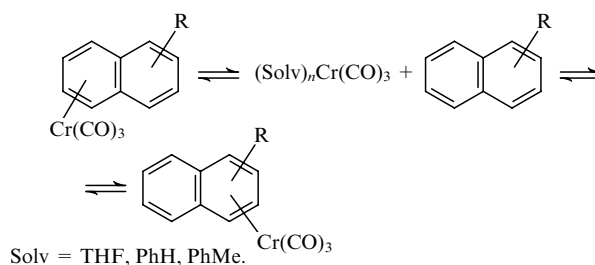
occurred under these conditions, the (η^6 -C₁₀D₈)Cr(CO)₃ complex was not formed. According to the data of mass spectrometry with the use of chemical ionisation, heating of (η^6 -C₁₀H₈)Cr(CO)₃ in the presence of perdeuterionaphthalene at $130\text{ }^{\circ}\text{C}$ (*i.e.*, at a temperature which is substantially higher than that required for IHR to proceed at a noticeable rate) for 6 h afforded only a small amount ($<5\%$) of (η^6 -C₁₀D₈)Cr(CO)₃.⁹³ However, in the reactions with the use of benzene derivatives (which coordinate the tricarbonylchromium group much more readily than polycyclic aromatic compounds) as the solvent, the migration of the Cr(CO)₃ group to monocyclic arene was observed even at $90\text{--}130\text{ }^{\circ}\text{C}$ and monocyclic complexes were obtained in yields of up to 20%. The complete replacement of naphthalene by monocyclic arene was achieved only upon heating of (η^6 -C₁₀H₈)Cr(CO)₃ in unsubstituted benzene ($140\text{ }^{\circ}\text{C}$, 6 h).

Therefore, even before IHR were found to occur in naphthalene complexes, investigations of these compounds have demonstrated that isomerisation can proceed according to both intramolecular and intermolecular mechanisms depending on the nature of the solvent. Later, the most convincing evidence that IHR in tricarbonylchromium complexes of monosubstituted naphthalenes proceeds through an intramolecular mechanism was obtained with the use of enantiomerically pure compounds.

Since chiral organometallic compounds are used in asymmetric synthesis and catalysis, they attract growing interest of researchers in organometallic chemistry.⁹⁷ Although the use of chiral compounds for studying the mechanisms of purely organic reactions has long been a classical method, this approach to investigation of the mechanism of IHR has been used only recently.⁹⁸ With the aim of elucidating the mechanism of η^6, η^6 -IHR in tricarbonylchromium complexes of naphthalene derivatives possessing planar chirality, the ability of their individual enantiomers to retain or lose optical activity in the course of the rearrangements was examined. If η^6, η^6 -IHR proceeds according to an intramolecular mechanism, the optical activity should be retained and isomeric complexes, for example, **39h** and **40h** (for which this process was studied in most detail), should be present in the equilibrium mixture only as either *R* or *S* forms.



If the rearrangement proceeds through either a dissociation or exchange intermolecular mechanism, the individual enantiomer should undergo racemisation due to the equally probable attacks of the tricarbonylchromium group [free ('hot'), σ -bonded to the solvent molecule containing a heteroatom or π -bonded to the solvent molecule, which does not contain a heteroatom (benzene or toluene)] on the arene from opposite sides. In this case, both



isomeric complexes containing the $\text{Cr}(\text{CO})_3$ group in either substituted or unsubstituted ring should be present in the equilibrium mixture both as the *R* and *S* forms.

Some planar-chiral tricarbonylchromium complexes of substituted naphthalenes can be separated by HPLC on an optical Chiracel OD column (Diacel, Japan).⁹⁹ Previously,¹⁰⁰ it had been demonstrated that this column, with modified cellulose as the support, is very efficient for separation of enantiomers of transition metal complexes, including tricarbonylchromium complexes of arenes.¹⁰¹ For a number of complexes of monosubstituted naphthalenes, very high selectivity factors of separation (α)

$$\alpha = \frac{t_2 - t_0}{t_1 - t_0},$$

were achieved, where t_0 is the retention time of the compound not retained (3.35 min) and t_1 and t_2 are the retention times of the enantiomers, which are eluted successively. For example, the selectivity for the complex **40b** was 5.23! The results of HPLC are given in Table 5.

Table 5. Data on separation of enantiomers of tricarbonylchromium complexes of naphthalene derivatives by HPLC on a Chiracel OD column.

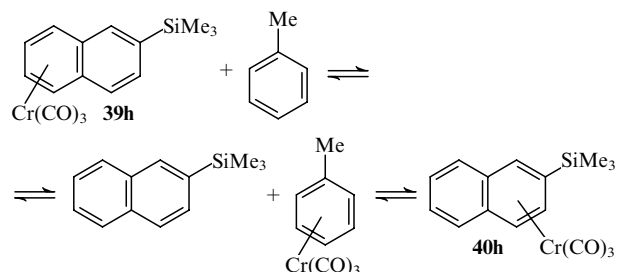
Complex 39	t_1 /min	t_2 /min	α	Complex 40	t_1 /min	t_2 /min	α
l	13.32	14.00	1.07	j	9.65	10.35	1.11
f	11.30	11.30	1.00	f	11.53	12.32	1.09
h	7.33	8.66	1.33	h	6.00	14.66	4.27
j	8.65	10.64	1.37	b	6.53	20.00	5.23
k	12.00	17.37	1.62	i	10.00	14.30	1.65
e	12.2	14.69	1.28	e	11.66	18.00	1.76
i	7.34	8.00	1.16	a	8.53	15.20	2.29
g	6.26	8.06	1.62	g	6.66	9.35	1.81

Note. The rate of the mobile phase [9 : 1 (v/v) n-hexane – propan-2-ol] was 10 ml min⁻¹.

To elucidate the mechanism of IHR in the tricarbonylchromium complexes of monosubstituted naphthalenes, **39h** and **40h**, the possibility of their enantiomers retaining optical activity in the course of the rearrangements (85 °C, C_6F_6 or toluene or C_6F_6 with 5% of THF) was examined. The chromatogram (Fig. 1*a*) of one

of the enantiomers of the complex **39h** in C_6F_6 was obtained. [It should be noted that the absolute configuration was determined (for example, by X-ray diffraction analysis) for none of the complexes.] As the inter-ring haptotropic rearrangement proceeds (C_6F_6 , 85 °C, 40 h), two intense peaks appear on the chromatogram. One of them corresponds to an enantiomer of **39h** (peak 1) and the second peak corresponds to an enantiomer of **40h** (peak 2), *i.e.*, the $\mathbf{39h} \rightleftharpoons \mathbf{40h}$ equilibrium occurs ($K_{\text{eq}} = [\mathbf{40h}]/[\mathbf{39h}] = 17.26$). The portions of enantiomers of **39h** (peak 3) and **40h** (peak 4) with another configurations were $\leq 1\%$ (Fig. 1*b*). Analogous results were obtained in the case of the $\mathbf{39h} \rightleftharpoons \mathbf{40h}$ rearrangement in decane.

The absence of racemisation proves that IHR in inert non-solvating solvents through an intramolecular mechanism without participation of dissociation and exchange processes. In this case, the $\text{Cr}(\text{CO})_3$ group ‘slips’ along the plane of the π -ligand, bonding with the ligand being retained. However, the degree of racemisation in pure toluene under the same conditions is $\sim 20\%$ (Fig. 1*c*), *i.e.*, IHP in aromatic solvents proceeds to some extent through an intermolecular exchange mechanism.



In the reaction performed under the same conditions but in C_6F_6 with the addition of 5% of THF, the complexes **39h** and **40h** underwent virtually complete racemisation ($\geq 75\%$) (Fig. 1*d*). For some other complexes, analogous results were achieved upon addition of 10% of dibutyl ether to C_6F_6 . Therefore, thermally induced η^6, η^6 -IHR in tricarbonylchromium complexes of naphthalene derivatives in the presence of solvating solvents proceeds primarily by the dissociation intermolecular mechanism.

The use of chiral complexes shows considerable promise for elucidation of fine details of the mechanism of organometallic reactions, in particular, IHR. For example, studies of racemisation of some complexes in the course of their rearrangements made it possible to determine the kinetic and thermodynamic parameters of IHP in the cases where these parameters cannot be obtained by other methods.

Based on the results of calculations by the extended Hückel method, Albright *et al.*⁴⁷ suggested that the presence of an exocyclic double bond should substantially promote η^6, η^6 -IHR in tricarbonylchromium complex of acenaphthylene **5**. The authors attempted to detect degenerate η^6, η^6 -IHR by dynamic NMR spectroscopy upon heating of the complex **5** in deuteriocalin to 160 °C. However, no broadening of lines caused by migration of the tricarbonylchromium group between the equivalent six-membered rings was observed. Apparently, the activation barrier is such that this rearrangement cannot be studied by two-dimensional NMR spectroscopy. However, the rearrangement can be examined without introduction of a label into the coordinated ring. The enantiomers of the complex **5** can be separated and each isomer should undergo racemisation in the course of IHR, which, in principle, allows one to determine the rate constant of the rearrangement as the rate constant of racemisation.

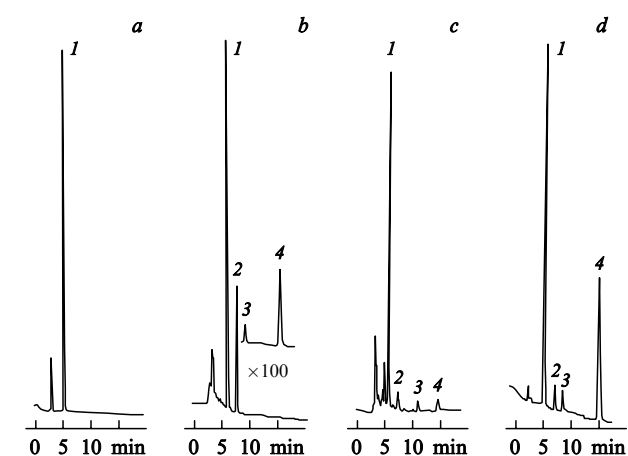
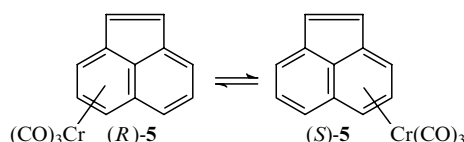


Figure 1. Chromatograms (HPLC on a Chiracel OD column) of the enantiomers of **39h** in C_6F_6 without heating (*a*) and with heating at 85 °C for 40 h in C_6F_6 (*b*), toluene (*c*) and the C_6F_6 –THF system (95 : 5) (*d*). Peaks (1) and (4) correspond to enantiomers of **39h** and peaks (2) and (3) correspond to enantiomers of **40h**. The integrated intensities of peaks (1) and (4) and of peaks (2) and (3) on the chromatogram (*d*) are equal.

1. η^6, η^6 -Rearrangements in tricarbonylchromium complexes of naphthalene derivatives

The kinetics of IHR in a number of tricarbonylchromium complexes of monosubstituted naphthalenes was studied by NMR spectroscopy. The rearrangements were performed in C_6F_6 at 85 °C.⁹⁴ The $^2H\{^1H\}$ NMR spectra of the deuterium-containing complexes **39c,d** and **40c,d** were measured. For the remaining complexes **39** and **40**, the ^1H NMR spectra were recorded. The signals in the NMR spectra were repeatedly integrated and averaged.

Kinetic studies demonstrated that the parameters obtained are well reproduced for pairs of the complexes, which differ in the position of the $Cr(CO)_3$ group, and are independent of a particular isomer chosen as the starting one. The typical kinetic curves for a pair of the complexes **39g** and **40g** are shown in Fig. 2.

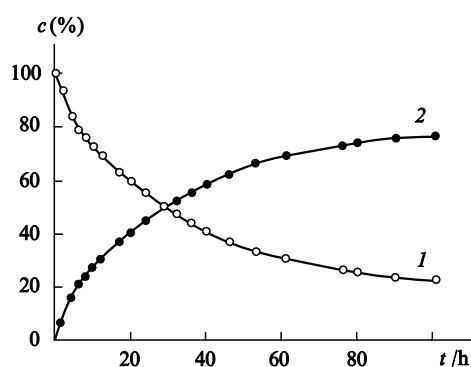
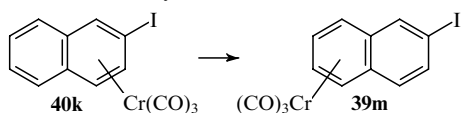


Figure 2. Kinetic curves of isomerisation of the tricarbonylchromium complexes of 1-trimethylsilylnaphthalene **39g** (**1**) and **40g** (**2**) (starting from **39g**).

The 2-iodonaphthalene complex **40k**, unlike the remaining tricarbonylchromium complexes of substituted naphthalenes, was demonstrated to be irreversibly rearranged to the isomeric complex **39m**. However, attempts to measure the kinetic parameters of the rearrangement failed due to instability of both complexes in all solvents under study.

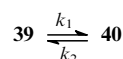


It should be noted that no noticeable destruction of the remaining compounds accompanied by the appearance of free ligands in the reaction mixtures was observed. In all cases, the rearrangements

Table 6. Rate constants, equilibrium constants and free activation energies of IHR in the complexes **39** (C_6F_6 , 85 °C).⁹⁴

Complex	$10^5 k_1$ /s ⁻¹	$10^5 k_2$ /s ⁻¹	K_{eq}	$\Delta G^\ddagger(358)$ /kcal mol ⁻¹
39e	0.90 ± 0.01	0.51 ± 0.02	1.77	29.4 ± 0.6
39f	1.82 ± 0.10	1.01 ± 0.10	1.80	29.2^a
39f	3.02 ± 0.24	1.45 ± 0.07	2.09	28.5 ± 1.2
39g	2.40 ± 0.02	0.50 ± 0.02	4.80	28.7 ± 0.7
39h	1.93 ± 0.03	0.11 ± 0.01	17.26	29.1 ± 0.6
39i	0.70 ± 0.01	0.14 ± 0.01	5.00	29.5 ± 0.5
39j	2.24 ± 0.04	0.17 ± 0.01	13.26	28.8 ± 0.7
39k	0.15 ± 0.01	4.36 ± 0.06	0.034	30.6 ± 0.4
39l	0.40 ± 0.01	3.46 ± 0.06	0.12	30.2 ± 0.8

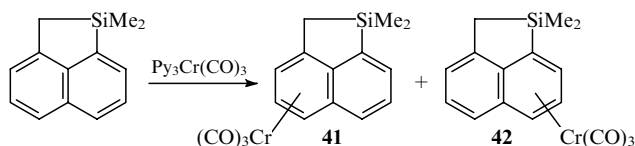
^a Calculations were performed based on the data reported in Ref. 83; cyclohexane- d_{12} was used as the solvent.



are described with a high degree of accuracy by a model of a reversible first-order reaction. The kinetic and thermodynamic parameters of the rearrangements of the complexes **39** in solutions in C_6F_6 are given in Table 6.

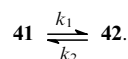
2. η^6, η^6 -Rearrangements in tricarbonylchromium complexes of naphthalene-related ligands

The kinetics of rearrangements in isomeric (η^6 -dimethylsilaacenaphthene)tricarbonylchromium complexes **41** and **42**, related to naphthalene complexes, was studied. The complexes **41** and **42** were prepared starting from dimethylsilaacenaphthene by the Öfele reaction in 76% yield.¹⁰²



The **41** : **42** ratio was equal to 1 : 6. *i.e.*, as discussed above, the tricarbonylchromium group tends to occupy the position in the ring containing an electron-donating substituent. Under conditions of TLC, the complexes **41** and **42** are characterised by virtually identical mobilities due to which they were separated by HPLC.

At 75–130 °C, the kinetically less stable complex **41** in C_6F_6 underwent rearrangement to the thermodynamically more stable complex **42**.



The content of the complex **42** in the equilibrium mixture was higher than 70%, which made it possible to measure a large number of points for the time dependence of the concentration, thus improving the accuracy and reliability of the experimental data. The kinetic data measured for the forward and back processes agree well with each other.¹⁰³

The relative concentrations of the complexes **41** and **42** were determined by repeated integration followed by averaging of the well-resolved signals for the protons of the methyl groups in the ^1H NMR spectra. The measurements were carried out in the temperature range of 105–118 °C because the rate of IHR at temperatures below 100 °C is very low, whereas at temperatures above 118 °C the complexes decompose (in the NMR spectrum, a signal for the protons of the methyl groups of the ligand appears at δ 0.52). The dependence of the concentration of the isomer **42** on the time (t) was calculated according to the equation for a reversible first-order reaction:¹⁰⁴

$$\ln \left(\frac{A_0 - A_e}{A_t - A_e} \right) = (k_1 + k_2) \Delta t,$$

where A_e , A_0 and A_t are the equilibrium, initial and actual concentrations of the complex **42**, respectively. The linear kinetic dependences were processed by the least-squares method. The kinetic dependences in the above-mentioned temperature range are shown in Fig. 3. The rate constants for the back and forward reactions **41** $\rightleftharpoons$ **42** are given in Table 7. The activation parameters of this rearrangement are given below.

Reaction	E_a /kcal mol ⁻¹	$\Delta H^\ddagger$ /kcal mol ⁻¹	$\Delta S^\ddagger$ /e.u.	$\Delta G^\ddagger$ /kcal mol ⁻¹
41 $\rightarrow$ 42	26.9 ± 0.8	26.1 ± 0.8	-8.1 ± 0.2	30.0 ± 1.0
42 $\rightarrow$ 41	26.7 ± 0.8	25.9 ± 0.8	-10.4 ± 0.2	30.5 ± 1.0

These results agree well with those reported in the literature for the related systems, in particular, for tricarbonylchromium complexes of methyl-⁸³ and methoxynaphthalenes.⁸⁴ The results of studies are unambiguously indicative of the absence of the

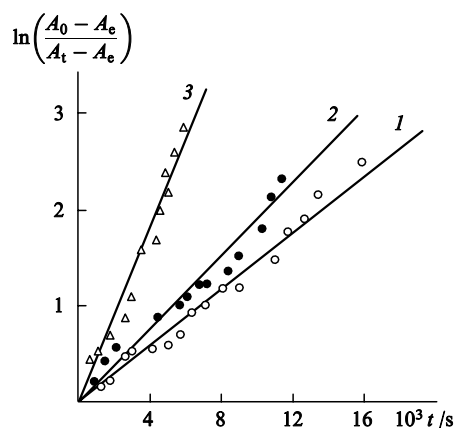


Figure 3. Kinetic first-order dependences obtained for IHR in the tricarbonylchromium complexes of η^6 -dimethylsilaacenaphthene **41** and **42** (starting from **41**) at 105 (**1**), 110 (**2**) and 118 °C (**3**).

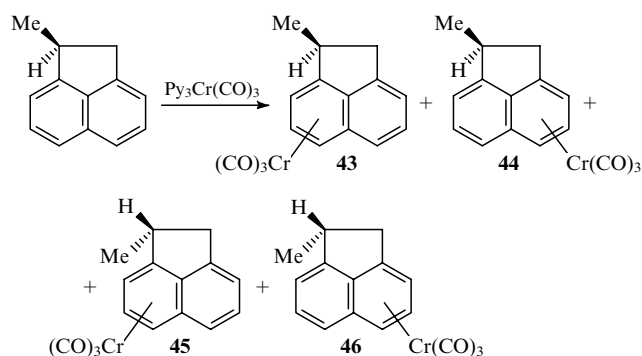
Table 7. Rate constants of IHR in the tricarbonylchromium complexes of η^6 -dimethylsilaacenaphthene **41** and **42**.

Rate constant $/s^{-1}$	Temperature /°C			
	85	105	110	118
$10^5 k_1$	1.15 ± 0.10^a	11.8 ± 0.4	14.0 ± 1.2	37.3 ± 1.1
$10^5 k_2$	0.64 ± 0.06^a	5.1 ± 0.2	5.80 ± 0.5	7.68 ± 0.8

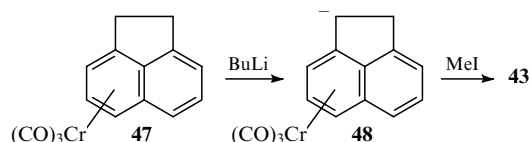
^a The rate constants were calculated taking into account the thermodynamic parameters.

contribution of the intermolecular dissociation mechanism to the IHR under examination. This is also confirmed by the relatively small negative entropies of activation both of the back and forward reactions because dissociation processes are generally characterised by higher negative $\Delta S^\ddagger$ values.⁶¹

The η^6, η^6 -inter-ring haptotropic rearrangements in a number of naphthalene-related tricarbonylchromium complexes in degassed anhydrous decane (an inert nonsolvating solvent) were examined.^{105, 106} For example, four possible isomeric tricarbonylchromium η^6 -complexes **43**–**46** (two isomers with the *exo* configuration of the methyl group and two isomers with the *endo* configuration) were obtained starting from 1-methylacenaphthene under the conditions of the Öfele reaction¹⁰⁵ in 37% total yield; the **43** : **44** : **45** : **46** ratio was 1 : 1 : 0.8 : 0.7. The complexes **43** and **44** were isolated in the individual state by HPLC. Attempts to separate the complexes **45** and **46** failed, but their mixture enriched with the isomer **45** was obtained (**45** : **46** = 3 : 1).

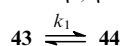


The individual complex **43** was prepared by deprotonation of (η^6 -acenaphthene)tricarbonylchromium (**47**) followed by the reaction of the resulting anion **48** with MeI.



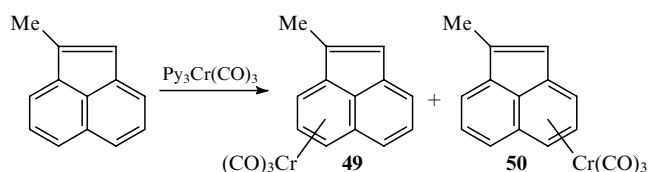
The electron-withdrawing tricarbonylchromium group substantially increases the acidity of the protons bound to the sp^3 -hybridised carbon atoms as a result of which deprotonation proceeds regioselectively only at the CH_2 group that is located more closely to the substituted ring. The reaction of the anion **48** with MeI is stereoselective. The methyl group attacks the negatively charged carbon atom from the side opposite to the bulky tricarbonylchromium group. The low yield (23%) of the target product **43** indicates that the anion **48** is unstable and decomposes to form, apparently, the corresponding carbanion. This agrees with the fact that 1-methylacenaphthene was isolated from the reaction mixture in a substantial amount. Previously, the stereo- and regioselectivity of such reactions was established for derivatives of fluorene⁷⁸ and indene⁷⁹ by ^1H NMR spectroscopy (the ASIS effect) and X-ray diffraction analysis. In the case of the complex **43**, irradiation of the methyl multiplet in the nuclear Overhauser effect (NOE) experiment led to an increase in the intensity of the corresponding doublet for the protons of the coordinated ring, which proves that the methyl group is located in the vicinity of this ring. In addition, the signal for the protons of the methyl group in the complex **43** is observed at higher field than those in the complexes **44**–**46**. Based on the ASIS effect,^{70, 79} this fact is indicative of the *exo* structure of **43**.

The η^6, η^6 -inter-ring haptotropic rearrangement

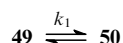


proceeded in solution in decane at 90 °C with a noticeable rate [$k_1 = 1.00 \times 10^{-5} s^{-1}$, $K_{eq} = 1.13$, $\Delta G^\ddagger(363) = 29.7 kcal mol^{-1}$] with retention of the *exo* configuration of the methyl group. Under the same conditions, the rearrangements of the complexes **45** and **46** proceeded with retention of the *endo* configuration of the methyl group. Isomerisation was monitored by HPLC. The addition of 10% of THF to decane resulted in the formation of a mixture of all four possible stereoisomers without regard to the particular isomer used as the starting compound. This is unambiguous evidence that the rearrangements in a nonsolvating medium proceed through an intramolecular mechanism, whereas the rearrangements in the presence of solvating solvents occur according to an intermolecular mechanism.¹⁰⁵ These results agree with the data of more recent studies confirming the retention of optical activity of enantiomerically pure tricarbonylchromium complexes of naphthalene derivatives in the course of η^6, η^6 -IHR.⁹⁸

The η^6, η^6 -inter-ring haptotropic rearrangements in isomeric tricarbonylchromium complexes of methylacenaphthylene (**49** and **50**) were examined.¹⁰⁶ A mixture of these complexes was obtained by the Öfele reaction in 78% yield (the **49** : **50** ratio was 45 : 55). The compounds **49** and **50** were isolated in pure form by HPLC.



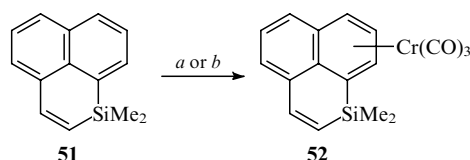
The necessity of studying IHR in methylated derivatives of tricarbonylchromium complexes of acenaphthylene stems from the fact that attempts to introduce a label directly into the six-membered ring of (η^6 -acenaphthylene)tricarbonylchromium (**5**)¹⁰⁷ [as in the case of tricarbonyl(η^6 -naphthalene)chromium] failed. The course of isomerisation



in solution in decane at 90 °C was monitored by NMR spectroscopy and HPLC. The rearrangement proceeded somewhat more rapidly [$k_1 = 2.29 \times 10^{-5} \text{ s}^{-1}$, $K_{\text{eq}} = 1.18$, $\Delta G^\ddagger(363) = 29.1 \text{ kcal mol}^{-1}$] than those in the case of analogous acenaphthene or naphthalene complexes. This fact agrees with the results of theoretical analysis.⁴⁷ In the cited study, potential energy surfaces were calculated by the extended Hückel method and it was demonstrated that the presence of an exocyclic double bond in the polyaromatic ligand should lead to a decrease in the activation barrier to IHR.

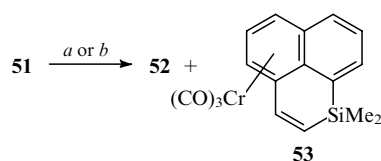
1,1-Dimethyl-1-silaphenalene (**51**) also contains an exocyclic double bond and two different aromatic fragments suitable for coordination to the transition metal atom. Hence, one would expect that η^6, η^6 -IHR will also readily proceed in the corresponding isomeric tricarbonylchromium complexes.

The compositions of the products of the reaction of 1,1-dimethyl-1-silaphenalene (**51**) with chromium carbonyls performed under different conditions were examined.¹⁰⁸ It was found that the reaction of the compound **51** with $(\text{NH}_3)_3\text{Cr}(\text{CO})_3$ in boiling dioxane or with $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ in boiling THF afforded complex **52** as the only product. According to the data of ^1H and ^{13}C NMR spectroscopy, the tricarbonylchromium group in the complex **52** is coordinated at the silicon-substituted ring.



- (a) $(\text{NH}_3)_3\text{Cr}(\text{CO})_3$, dioxane, 100 °C (42%);
(b) $(\text{MeCN})_3\text{Cr}(\text{CO})_3$, THF, 64 °C (6%).

Both possible isomers **52** and **53** were formed only when the reaction temperature was decreased. The reaction of the compound **51** with $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ at 34 °C gave rise to a mixture of the complexes **52** and **53** in a total yield of $\leq 1\%$. The reaction of the compound **51** with $\text{Py}_3\text{Cr}(\text{CO})_3$ at 0 °C afforded a mixture of the isomers in 54% yield with the complex **53** predominating.



- (a) $(\text{MeCN})_3\text{Cr}(\text{CO})_3$, 34 °C (1%) (**52**:**53** = 3:2);
(b) $(\text{Py})_3\text{Cr}(\text{CO})_3$, 0 °C, 1 h (54%) (**52**:**53** = 2:3).

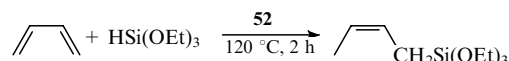
This is yet another example of the effect of thermodynamic and kinetic factors on the formation of tricarbonylchromium complexes with polycyclic aromatic ligands.

The complexes **52** and **53** were identified by ^1H and ^{13}C NMR spectroscopy and mass spectrometry. Since the complex **53**, unlike the complex **52**, is unstable under conditions of TLC, it was not isolated in pure form. The complex **52** decomposes upon storage of a mixture of the complexes even in the solid state.

Heating of a mixture of the complexes **52** and **53** in the C_6F_6 – C_6D_{12} system or in heptane to 90 °C for 5 h resulted in the complete rearrangement of the complex **53** to form the thermodynamically more stable complex **52**. The absence of traces of the free ligand in the reaction mixture and the fact that the rearrangement proceeds in nonpolar media are indicative of an intramolecular mechanism of IHR. The reverse **52** $\rightarrow$ **53** rearrangement was observed in none of the experiments.

The rearrangements of silaphenalene complexes proceed under milder conditions than the rearrangements of silaacenaph-

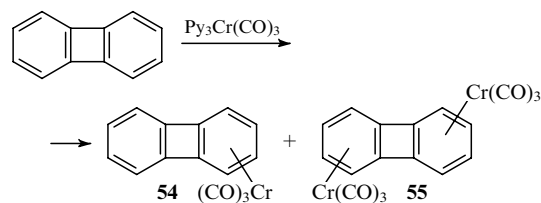
thene complexes. This is indicative of a decrease in the activation energy of the process, although the rate constant of this process was not estimated. It should be noted that the isomer in which the tricarbonylchromium group is coordinated at the silicon-substituted ring is thermodynamically more stable in the case of the silaphenalene complexes **52** and **53** and the silaacenaphthene complexes **41** and **42**. The complex **52** acts as a catalyst of hydrosilylation of butadiene. The catalytic action is achieved upon addition of 0.2% of the compound **52** to an equimolar mixture of diene and silane.¹⁰⁹ The characteristic feature of the reaction is its regio- and stereospecificity. Hydrosilylation afforded (*Z*)-1-triethoxysilylbut-2-ene as the only product in a yield of $\geq 90\%$. Its structure was established by ^1H and ^{13}C NMR spectroscopy.¹⁰⁹



The catalytic activity of tricarbonylchromium complexes of polycyclic arenes (naphthalene, phenanthrene and anthracene) in hydrogenation of conjugated dienes and acetylenes, isomerisation of dienes, Kharasch addition of CCl_4 to alkynes, *etc.* was attributed to the ability of the tricarbonylchromium group, which is η^6 -bonded to the arene ring, to change the mode of bonding to form an η^4 -intermediate.¹¹⁰

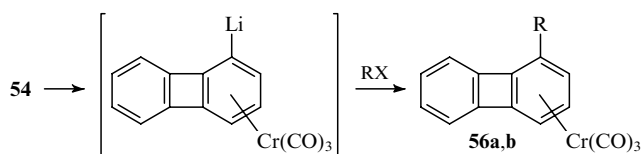
3. η^6, η^6 -Rearrangements in tricarbonylchromium complexes of biphenylene

Tricarbonylchromium complexes of biphenylene are of considerable interest from the viewpoint of studies of η^6, η^6 -IHR. The η^6 -mononuclear (**54**) and η^6 -binuclear (**55**) tricarbonylchromium complexes of biphenylene were synthesised by the Öfele reaction in 66% total yield (**54**:**55** = 15.5:1).¹⁰⁶ The individual complexes were isolated from the reaction mixture by TLC.



Previously, the complexes **54** and **55** were obtained in the reaction of biphenylene with $(\text{NH}_3)_3\text{Cr}(\text{CO})_3$ in boiling dioxane in a similar ratio.^{111,112} It was assumed that the binuclear complex **55**, like the structurally similar binuclear complex of fluorene,⁷⁸ contains the $\text{Cr}(\text{CO})_3$ group in the *trans* position because such a structure was established for the biphenylene binuclear complex of molybdenum $\eta^6, \eta^6\text{-C}_{12}\text{H}_8[\text{Mo}(\text{CO})_3]_2$ by X-ray diffraction analysis.¹¹³

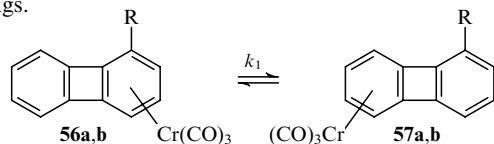
The directed introduction of substituents into the coordinated ring was performed by a procedure analogous to that used in the case of tricarbonyl(η^6 -naphthalene)chromium. Metallation of the complex **54** with butyllithium in THF proceeded regio- and stereoselectively to form complexes **56a,b** in which the label is located exclusively at position 1 of the coordinated ring.



R = D (**a**), Me (**b**).

The η^6, η^6 -inter-ring haptotropic rearrangements in tricarbonylchromium complexes of 1-substituted biphenylenes **56a,b** containing the planar ligand (according to the data of X-ray diffraction analysis) proceed more slowly than the corresponding

rearrangements in monosubstituted naphthalene complexes. Thus, the isomers **57a,b** were detected in the reaction mixture obtained upon heating of the complexes **56a,b** only at temperatures above 100 °C, IHR proceeding with a noticeable rate at 120 °C. In the course of the rearrangement, the tricarbonylchromium group migrates between the nonequivalent six-membered rings.

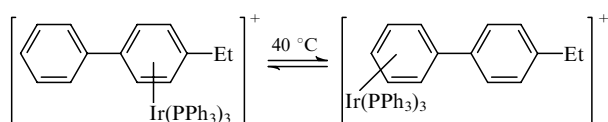


R = D (**a**), Me (**b**).

According to the data of ^2H NMR spectroscopy, the equilibrium for the deuterium-containing complexes **56a** and **57a** in decane was established at 120 °C in 6 h [$k_1 = 4.79 \times 10^{-5} \text{ s}^{-1}$, $K_{\text{eq}} = 1.00$, $\Delta G^\ddagger(393) = 31.00 \text{ kcal mol}^{-1}$]. The η^6, η^6 -rearrangements in the methyl-substituted complexes **56b** and **57b** proceeded somewhat more slowly [$k_1 = 3.41 \times 10^{-5} \text{ s}^{-1}$, $K_{\text{eq}} = 1.10$, $\Delta G^\ddagger(393) = 31.25 \text{ kcal mol}^{-1}$].

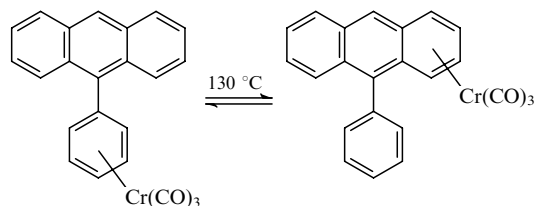
4. Synthesis of tricarbonylchromium complexes of substituted biphenyls and studies of the mechanism and kinetics of rearrangements in these complexes

Until the mid-1980s, the data on IHR in complexes with bi- or polycyclic open ligands were virtually lacking in the literature. Biphenyl complexes represent the simplest model systems.^{114–116} More complex analogues, *viz.*, tricarbonylchromium complexes of 1,3,5-triphenylbenzene,¹¹⁷ triphenylene,¹¹⁸ 9-phenylanthracene,¹¹⁹ 9,10-dihydrophenanthrene,¹²⁰ siloxaphenanthrene,¹²¹ 9,9-dimethyl-9-silafluorene,¹²² fluorene,⁷⁴ carbazole⁷⁴ and fluoranthene,^{91,123} were also prepared. Procedures for the introduction of a label into tricarbonylchromium complexes of biphenyl derivatives are scarce. [The only procedure for the introduction of a label into (η^6 -biphenyl)tricarbonylchromium involving the reaction of its stannylated derivative with butyllithium has been reported.¹²⁴] Only two examples of rearrangements in complexes of biphenyl and its derivatives with transition metals were described before 1985. The inter-ring haptotropic rearrangement in the ethylbiphenyl complex of iridium was described in the study¹²⁵ with reference to the Ph. D. Thesis of Mellea.¹²⁶



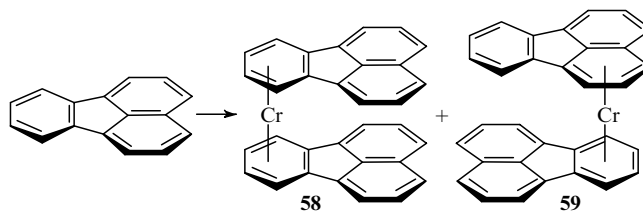
The reaction proceeded under mild conditions (40 °C) and the equilibrium ratio of the isomers was 1 : 1.

Isomerisation of tricarbonylchromium complexes of 9-phenylanthracene¹¹⁹ proceeded under more drastic conditions (dibutyl ether, 130 °C). The tricarbonylchromium group successively migrates first over the biphenyl system and then over the fused system to the peripheral rings.¹¹⁹ The mechanism of this rearrangement is not entirely known. Although the authors assumed that the rearrangement proceeds through an intermolecular mechanism, this statement is questionable and calls for special studies.

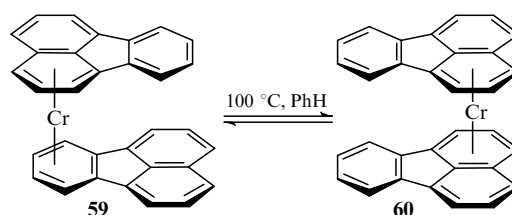


Recently, the first example of η^6, η^6 -IHR in sandwich chromium complexes was reported.¹²⁷ The vapour-phase (350 °C)

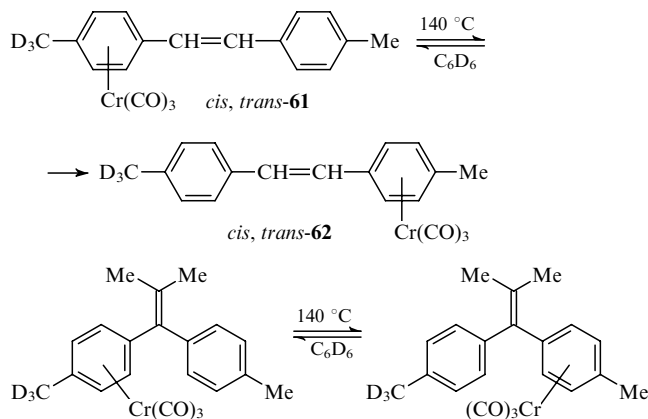
reaction of fluoranthene with metal vapour was demonstrated to afford complex **58** as the major product along with isomeric complex **59**. In the former complex, the chromium atom is located at the benzene rings, whereas one ligand in the complex **59** is coordinated at the 'naphthalene' fragment.



Prolonged heating (for several days) of the isomer **59** in deuteriobenzene at 100 °C resulted in the reversible rearrangement to form complex **60** in which both ligands are coordinated at the 'naphthalene' fragment, *i.e.*, η^6, η^6 -IHR of the biphenyl type occurred.



Migrations of the $\text{Cr}(\text{CO})_3$ group in biphenyl-related open systems, *viz.*, in tricarbonylchromium complexes of diphenylalkanes [$(\eta^6\text{-Ph})\text{Cr}(\text{CO})_3(\text{CH}_2)_n\text{Ph}$ ($n = 1-4$), unsymmetrically substituted *cis*- and *trans*-stilbenes and 1,1-diarylethylenes, were observed.^{128,129} At 140 °C, the $\text{Cr}(\text{CO})_3$ group in complexes of substituted stilbenes (**61** and **62**) and diarylethylenes migrates between the rings containing the methyl and CD_3 groups.



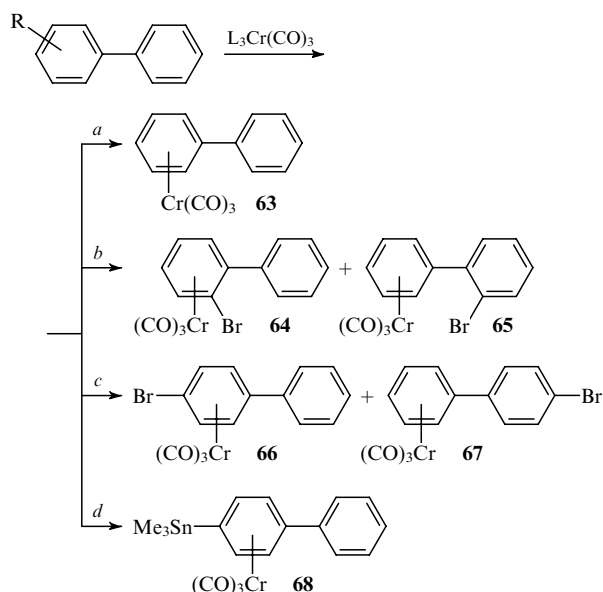
The rate of the intramolecular rearrangement is noticeably higher than that of the rearrangement proceeding through the dissociation mechanism, which is evidenced by an insignificant amount of products of replacement of the ligand in these complexes by the 'trapping' ligand.

The rate constants of IHR were determined for the *cis*- and *trans*-isomers of stilbene complexes at 140 °C. For the rearrangement **61** $\rightarrow$ **62** proceeding by an intramolecular mechanism, the rate constants are $4.20 \times 10^{-5} \text{ s}^{-1}$ and $6.95 \times 10^{-5} \text{ s}^{-1}$ for the *trans*- and *cis*-isomers, respectively. The rate constants of exchange through a dissociation mechanism are substantially smaller ($0.18 \times 10^{-5} \text{ s}^{-1}$ and $0.066 \times 10^{-5} \text{ s}^{-1}$, respectively).

a. Synthesis of tricarbonylchromium complexes of substituted biphenyls

It was not until 1985 that progress was achieved in the synthesis of tricarbonylchromium complexes of biphenyl derivatives labelled at one of the rings. For this purpose, insignificantly modified

procedures, which had been developed primarily for the synthesis of tricarbonylchromium complexes of monocyclic arenes, were used. The reactions of the ligands (biphenyl and 2-bromo-, 4-bromo- and 4-trimethylstannylbiphenyls) with chromium carbonyls $L_3Cr(CO)_3$ ($L = CO$,¹³⁰ NH_3 ,⁸⁷ or Py ;⁸⁸ $L_3 = C_{10}H_8$,⁴⁶) afforded complexes **63–68** in moderate yields (30%–40%).¹³¹



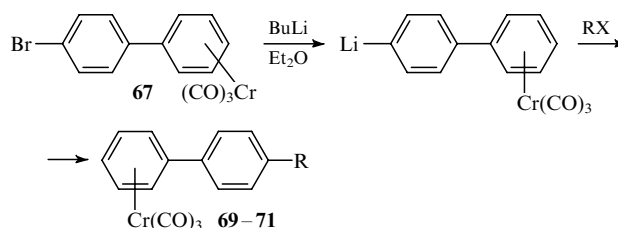
(a) $L = CO$, $R = H$, $Bu_2O:THF = 1:6$, $140^\circ C$, 4 h; (b) $L = CO$, $R = 2-Br$, $Bu_2O:THF = 1:5$, $140^\circ C$, 5 h; (c) $L = CO$, $R = 4-Br$, $Bu_2O:THF = 1:7$, $140^\circ C$, 7 h; (d) $L = NH_3$, $R = 4-SnMe_3$, dioxane, $100^\circ C$, 2 h.

Either both possible isomers or only one isomer are formed depending on the nature of the substituent in the ligand, its position and the type of chromium carbonyl used in the reaction. Thus the reaction of 4-trimethylstannylbiphenyl with $(NH_3)_3Cr(CO)_3$ gave rise exclusively to the complex **68**. Due to the strong electron-donating properties of the trimethylstannyl group, the electron density at the substituted ring increases resulting in coordination of the $Cr(CO)_3$ group at this ring. Analogously, the Rausch reactions of 2- and 4-bromobiphenyls with $(NH_3)_3Cr(CO)_3$ (dioxane, $100^\circ C$, 2 h) afforded only the complexes **65** or **67** containing the $Cr(CO)_3$ group in the unsubstituted ring due to the electron-withdrawing properties of bromine (kinetic control). Prolonged heating of the bromo derivatives **65** or **67** with $Cr(CO)_3$ in a mixture of dibutyl ether and THF at $140^\circ C$ (thermodynamic control) yielded a mixture of the isomers **64** and **65** or **66** and **67**, respectively, with the complex containing the bromine atom in the uncoordinated ring predominating. Although the isomers can be readily isolated by TLC, the above-considered procedure cannot be used for the preparative synthesis of complexes containing halogen in the coordinated ring.

Based on analysis of the above-considered results, it can be stated with assurance that individual complexes containing a substituent either in the uncoordinated or coordinated rings can be selectively prepared starting from bromo- or trimethylstannyl derivatives of biphenyl by the Rausch reaction. Subsequently, the bromine atom or the $SnMe_3$ group can be first replaced by lithium under the action of $BuLi$ and then by the R substituent by the reactions of the lithium derivatives with electrophilic reagents RX .

On the whole, the selective synthesis of tricarbonylchromium complexes of substituted biphenyls by the exchange reaction of bromine for lithium is analogous to the procedure used for the preparation of naphthalene complexes. The reaction of the complex **67** containing the tricarbonylchromium group in the unsubstituted ring with $BuLi$ in anhydrous ether at $-78^\circ C$ led to the replacement of Br by Li . The lithium derivative is stable at low temperatures and reacts rather smoothly with electrophiles (D_2O ,

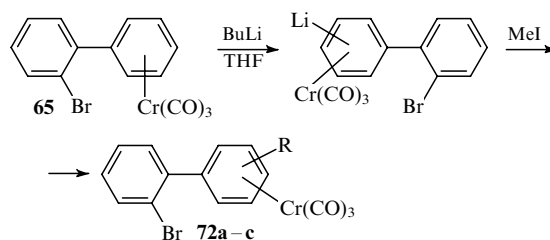
Me_3SnCl , MeI , etc.) at $0^\circ C$ to form selectively labelled complexes **69–71** containing the label at position 4 of the uncoordinated ring.¹³¹



$RX = D_2O$, Me_3SnCl , MeI ; $R = D$ (**69**), Me (**70**), Me_3Sn (**71**).

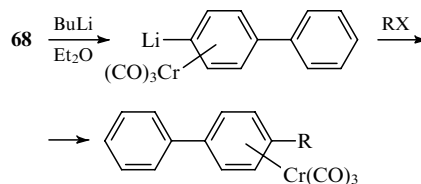
Attempts to prepare the corresponding complexes containing a label at position 2 of the uncoordinated ring starting from the compound **65** have not met with success even when the reactions were performed at room temperature, which is, apparently, due to steric hindrance to the replacement of Br by Li .

It should be noted that it is necessary to perform these reactions, like the synthesis of naphthalene complexes, in ether because direct metallation of the coordinated ring in THF proceeds more rapidly than the replacement of Br by Li . Thus the reaction of the derivative **65** with $BuLi$ in THF followed by treatment of the reaction mixture with methyl iodide gave rise to the complexes **72a–c** (**72a**:**72b**:**72c** = 13:57:30). The low content of the complex **72a** in the mixture is attributable to steric hindrances, which appear either in the stage of metallation or, what is less probable, in the stage of the reaction of the lithium derivatives with MeI .



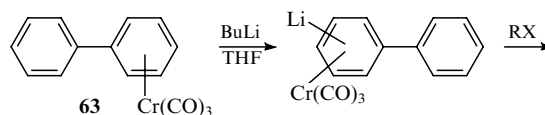
$R = 2-Me$ (a), $3-Me$ (b), $4-Me$ (c).

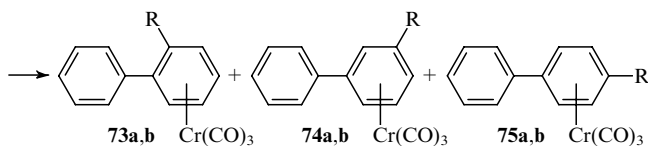
The replacement of the Me_3Sn group by lithium in the biphenyl complexes **68** was not performed. However, by analogy with the corresponding naphthalene complexes, complexes selectively substituted at the coordinated ring can be apparently prepared according to this procedure.



$RX = D_2O$, MeI , Me_3SiCl , etc.

The synthesis of tricarbonylchromium complexes of substituted biphenyls by direct metallation of $(\eta^6$ -biphenyl)tricarbonylchromium was described. Thus the reaction of the complex **63** with $BuLi$ in THF was accompanied by metallation of the coordinated ring. Then the reaction of the resulting lithium derivatives with the electrophile RX at $-78^\circ C$ afforded a mixture of all three possible isomers.¹³¹



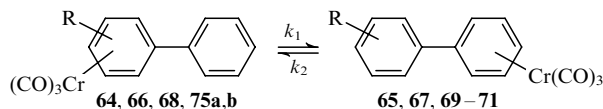


R = D (**a**), Me (**b**).

For example, the reactions of lithium derivatives with D₂O or MeI at $-78\text{ }^{\circ}\text{C}$ gave rise (according to the data of ²H NMR spectroscopy) to a mixture of deuterated complexes **73a**–**75a** in 84% total yield (**73a**:**74a**:**75a** = 10:65:25) or a mixture of methyl derivatives **73b**–**75b** in 17.5% total yield (**73b**:**74b**:**75b** = 12:58:30), respectively. The ratios of the isomers of deuterio- and methyl-containing derivatives are rather similar, which does not allow one to consider the effects of kinetic and thermodynamic control on their formation. Storage of the reaction mixture at $0\text{ }^{\circ}\text{C}$ for 1 h followed by treatment with MeI afforded only the isomer **73b**. Apparently, the 2-lithium-substituted derivative is the thermodynamically most stable compound and is predominantly formed through the replacement of H by Li. On the whole, the procedure for the synthesis involving metalation of the coordinated ring in the complex **63** is inferior to the above-described procedures (see Section III.1.b) in the preparative respect. However, the use of all available synthetic approaches enables one to prepare various tricarboxylchromium complexes of substituted biphenyls. It should be noted that in the general case these procedures are applicable to all polyaromatic arenes.

b. Studies of rearrangements in tricarboxylchromium complexes of substituted biphenyls

For all available tricarboxylchromium complexes of substituted biphenyls, the possibility of IHR was studied upon their heating in anhydrous oxygen-free decane in the temperature range of $140\text{--}174\text{ }^{\circ}\text{C}$ for 4–20 h.¹³¹



R = 4-SnMe₃ (**68**, **71**), 2-Br (**64**, **65**), 4-Br (**66**, **67**), 4-D (**69**, **75a**), 4-Me (**70**, **75b**).

The course of the rearrangement was monitored by withdrawing samples every 30 min and recording the ¹H NMR spectra (²H NMR spectra were measured for deuterated derivatives) to determine the isomer ratio. Heating was terminated if the isomer ratio ceased to change (according to the NMR data). In some cases, this approach made it possible to estimate the rate constants and equilibrium constants for IHR. The structures of the complexes were established by ¹H and ¹³C NMR spectroscopy.

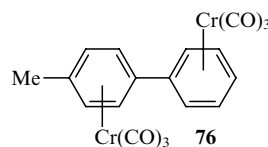
The inter-ring haptotropic rearrangements in the biphenyl complexes **64**, **66** and **68** are irreversible. Heating of the stannylated derivative **71** in boiling decane ($174\text{ }^{\circ}\text{C}$, 5.5 h) resulted in the complete migration of the Cr(CO)₃ fragment from the unsubstituted ring to the substituted fragment to form the complex **68** [$k_2 = 6.42 \times 10^{-5}\text{ s}^{-1}$, $\Delta G^\ddagger(447) = 35.10\text{ kcal mol}^{-1}$], whereas the corresponding isomeric complex **68** did not undergo rearrangement under these conditions, *i.e.*, the reaction is actually irreversible. At $174\text{ }^{\circ}\text{C}$, the tricarboxylchromium group in the 2- and 4-bromophenyl derivatives (**64** and **66**) migrates irreversibly from the substituted ring to the unsubstituted one in 13 and 6 h, respectively [$k_1 = 2.23$ and $5.13 \times 10^{-5}\text{ s}^{-1}$, $\Delta G^\ddagger(447) = 36.04$ and $35.3\text{ kcal mol}^{-1}$ for the complexes **64** and **66**, respectively]. Reverse migration of the tricarboxylchromium group was not observed, which is evidence in favour of the irreversibility of IHR. Analysis of the kinetic data demonstrated that the rearrangement in the 2-bromo derivative **64** proceeds much more slowly than that

in the 4-bromo derivative **66**. Apparently, this is due to steric interactions in the complex **64** existing between the bulky bromine atom, on the one hand, and the *ortho*-proton of the adjacent ring and the organometallic group, on the other hand, resulting in the appearance of a twisting angle (a nonzero dihedral angle) and distortion of conjugation of the phenyl rings (see, for example, Refs 132 and 133). Ceccon *et al.*¹³⁴ also revealed the presence of the twisting angle and a noticeable degree of noncoplanarity of the five- and six-membered rings in the tricarbonylchromium complexes **29** and **30**. For the thermodynamically more stable (and, correspondingly, more populated) conformation of the *ortho*-derivatives of (η^6 -biphenyl)tricarbonylchromium, the degree of noncoplanarity of the six-membered rings is higher than that in the corresponding *para*-derivatives. This effect is manifested in a substantial decrease in NOE between the protons of the coordinated and uncoordinated rings due to an increase in the average distance between their *ortho*-protons. The appearance of the nonzero dihedral angle between the benzene rings agrees with the data obtained by the DFT method for tricarbonyl(η^6 -2-chlorobiphenyl)chromium containing the Cr(CO)₃ group in the unsubstituted ring, which was chosen instead of the 2-bromo derivative to simplify calculations. In this compound, the dihedral angle is 58.14° and the halogen and chromium atoms are oppositely directed.¹³⁵

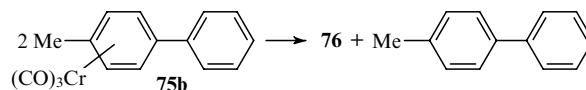
The results of quantum-chemical calculations with the use of the HyperChem program (the PM3 method) for uncoordinated biphenyl and 2-bromobiphenyl also confirm the above-considered experimental and theoretical data. According to these calculations, the biphenyl molecule is virtually planar (the dihedral angle is 0.2°), whereas the phenyl rings in 2-bromobiphenyl are essentially noncoplanar (the dihedral angle is 52.9°).

It should also be noted that the corresponding dihedral angle in the tricarboxylchromium complex of unsubstituted biphenyl (calculations by the DFT method) is 21.38° , *i.e.*, coordination to the transition metal atom leads to an increase in steric hindrance.¹³⁵

The inter-ring haptotropic rearrangements in 4-deuterated and 4-methyl derivatives of tricarboxylchromium complexes of biphenyl, unlike those in the corresponding trimethylstannyl and bromo derivatives, are reversible. Heating of the complexes **75a,b** in decane at $174\text{ }^{\circ}\text{C}$ for 5 and 8 h, respectively, resulted in reversible rearrangements to form the isomeric complexes **69** and **70**, respectively ($K_{\text{eq}} = [\text{75a}]/[\text{69}] = 1.0$ and $K_{\text{eq}} = [\text{75b}]/[\text{70}] = 1.4$). The binuclear complex **76** was isolated from a mixture of the 4-methylbiphenyl complexes **70** and **75b** (which was formed as a result of IHR) by TLC in 5% yield.



The structure of the compound **76** was established by mass spectrometry and ¹H NMR spectroscopy. The formation of **76** indicates that insignificant dissociation of the complexes with elimination of the tricarboxylchromium group that passes into solution did occur under drastic thermal conditions even in inert nonsolvating decane. An alternative explanation assumes that a bimolecular reaction proceeded giving rise to a molecule of the binuclear complex **76** and the ligand from two molecules of the complex **75b**.



Therefore, inter-ring haptotropic rearrangements in tricarboxylchromium complexes of biphenyl derivatives proceed through an intramolecular mechanism. However, due to the high temper-

atures of the reactions, an intermolecular mechanism is realised to a small extent. This conclusion is consistent with kinetic evidence that metallotropic rearrangements in tricarbonylchromium complexes of diphenylalkanes proceed predominantly by an intramolecular mechanism.^{128, 129}

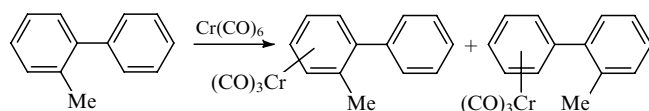
Analogous results were obtained upon heating of a mixture of the biphenyl complexes **73a**–**75a** containing deuterium in the coordinated ring in decane at 174 °C for 6 h. Under these conditions, the reversible rearrangement proceeded accompanied by migration of the tricarbonylchromium group from the deuterium-labelled ring to the deuterium-free ring. The ratio between the isomers containing deuterium in the coordinated and uncoordinated rings is close to unity in all three pairs of 2-, 3- and 4-deuterium-substituted complexes (according to the ^2H NMR data; acetone as the solvent).

When a mixture of complexes containing 2-, 3- and 4-methyl-substituted coordinated rings (**73b**–**75b**) was heated under the same conditions, only isomers **74b** and **75b** underwent rearrangements to form complexes containing substituents in the uncoordinated ring (K_{eq} is 1.6 and 1.4 for the isomers **74b** and **75b**, respectively).

The fact that IHR did not occur in the 2-methyl-substituted complex **73b**, as in the case of the corresponding bromo derivative, is attributable to the fact that the phenyl rings are essentially noncoplanar in the most populated rotamer. This is consistent with a decrease in NOE between the *ortho*-protons of the coordinated and uncoordinated rings in the complex **73b** (3%–4%) compared to the corresponding values obtained for the complexes **74b** and **75b** (7%–9%).

The dihedral angle in the 2-methylbiphenyl complex containing the $\text{Cr}(\text{CO})_3$ group in the unsubstituted ring calculated by the DFT method is 62.01°.¹³⁵

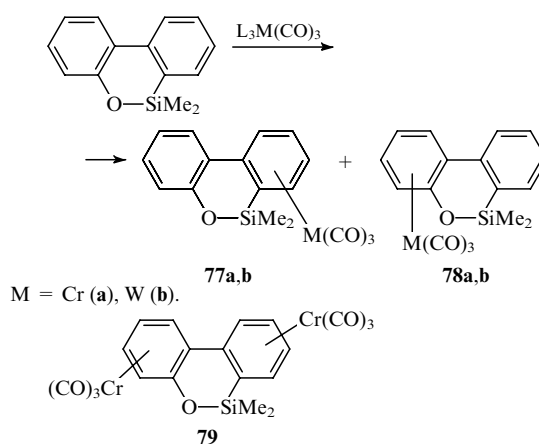
Interestingly, a mixture of 2-methyl-substituted complexes containing the $\text{Cr}(\text{CO})_3$ group either in the coordinated or uncoordinated rings did form from 2-methylbiphenyl and $\text{Cr}(\text{CO})_3$ upon refluxing in the dibutyl ether–THF system. The isomeric 2-methyl-substituted tricarbonylchromium complexes were separated by TLC. The isomer ratio (1.3 : 1) appeared to be similar to that obtained as a result of inter-ring haptotropic rearrangements in tricarbonylchromium complexes of 3- and 4-methyl-substituted biphenyls.



The absence of IHR in 2-methyl-substituted tricarbonylchromium complexes of biphenyl and the fact that their mixture can be readily obtained by the reaction of the ligand with chromium hexacarbonyl is additional evidence in favour of the intramolecular character of IHR. Therefore, a necessary condition of IHR to occur in complexes of substituted biphenyls and related ligands is a small degree of noncoplanarity of the rings (the dihedral angle should be smaller than 22°, as in the case of the biphenyl complex), which is impossible in 2-substituted complexes due to steric effects.

5. η^6, η^6 -Rearrangements in tricarbonylchromium complexes of biphenyl-related ligands

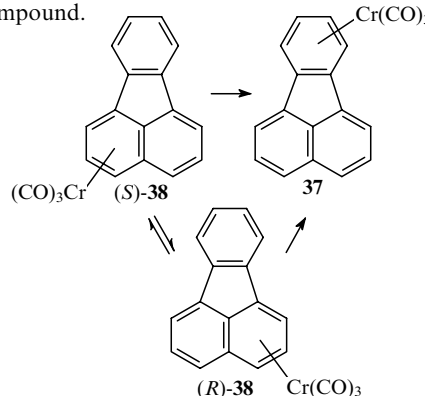
Biphenyl-related 10,10-dimethyl-10-sila-9-oxa-9,10-dihydrophenanthrene, which contains substituents possessing different electronic properties in both rings, is of interest. Tricarbonylchromium and -tungsten complexes of this compound were prepared by reactions with different chromium and tungsten carbonyls.^{121, 136} In the case of $\text{M} = \text{Cr}$, the bis(tricarbonyl)chromium complex $\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_{12}\text{H}_8\text{OSiMe}_2[\text{Cr}(\text{CO})_3]_2$ (**79**) was formed in a small amount.



The six-membered rings in the tricarbonylchromium complexes **77a** and **78a** are noncoplanar and the dihedral angles between these rings are (according to the X-ray diffraction data) 20.4° and 15.5°, respectively.¹³⁷

Heating of the complex **77a** in anhydrous degassed decane at 130 °C led to IHR yielding the isomer **78a**. The equilibrium was established in 6 h. According to the data of ^1H and ^{13}C NMR spectroscopy, the **77a** : **78a** ratio was 12 : 1 (the same isomer ratio was obtained upon heating of the complex **78a**). In both cases, the ^1H NMR spectra of the equilibrium mixtures have low-intensity signals belonging to the ligand and the binuclear complex **79**. However, their total amount was no higher than 5% even after heating of the reaction mixture at 174 °C for 20 h. The binuclear complex and the ligand were formed due to either thermal destruction or bimolecular reactions proceeding in the complexes **77a** and **78a**. Analogously (but under substantially milder conditions), the inter-ring haptotropic rearrangement proceeded in the tricarbonyltungsten complex **77b**. After heating of **77b** in decane at 100 °C for 6 h, the ^1H NMR spectrum had additional signals, which were assigned to the isomer **78b** (**77b** : **78b** = 15 : 1). Attempts to isolate the complex **78b** from the reaction mixture by TLC failed and the ^1H NMR spectrum of the pure complex was not measured.¹³⁶

Fluoranthene is of considerable interest because η^6, η^6 -IHR both of the 'biphenyl' and 'naphthalene' types can proceed in this compound.



In this case, the complex **38** exists as two enantiomers, which are interconverted in the course of the 'naphthalene' rearrangement. Apparently, the kinetic parameters of such degenerate rearrangements may be determined from the rates of racemisation of the corresponding enantiomers in the future.

Heating of the η^6, η^6 -fluoranthene complex **38** in which the $\text{Cr}(\text{CO})_3$ group is located at the naphthalene fragment even at rather low temperature (in decane or benzene at 100 °C for 10 h) led to IHR to form the complex **37** in which the $\text{Cr}(\text{CO})_3$ group is located at the benzene ring.^{91, 123} On the contrary, prolonged heating (> 100 h) of the complex **38** under the same conditions did not give rise to the isomer **37**. The inter-ring haptotropic

rearrangement was not accompanied by substantial decomposition of the complexes or migration of the $\text{Cr}(\text{CO})_3$ group to the benzene ring, which is consistent with the results of other studies.^{46,90} It was demonstrated that when tricarbonyl(η^6 -naphthalene)chromium was heated in benzene, the migration of the tricarbonylchromium group to the benzene ring proceeded with a noticeable rate ($k_{\text{sub}} = 1.73 \times 10^{-4} \text{ s}^{-1}$)⁴⁶ only at 140 °C and was completed in 6 h.

The rate constant of the irreversible η^6, η^6 -inter-ring haptotropic rearrangement $38 \rightarrow 37$ was determined from the data of ^1H NMR spectroscopy (C_6F_6 as the solvent). The corresponding kinetic curves are shown in Figs 4 and 5. The rate constant of the rearrangement is equal to $(5.5 \pm 0.2) \times 10^{-6} \text{ s}^{-1}$; $E_a = 30.13 \text{ kcal mol}^{-1}$. The complexes **37** and **38** were separated by TLC and their structures were established by ^1H and ^{13}C NMR spectroscopy and X-ray diffraction analysis.

Therefore, IHR in planar fluoranthene complexes proceed under substantially milder conditions (80–90 °C) than those in open biphenyl complexes (even in the cases of 4-bromo- or 4-methyl-substituted complexes, IHP started at temperatures above 130 °C). At 100 °C, the replacement of the fluoranthene ligand by C_6D_6 in the course of η^6, η^6 -IHR was not observed. This replacement was achieved only at 130 °C. After 10 h, the ligand: $\text{C}_6\text{D}_6\text{Cr}(\text{CO})_3$ ratio reached 1:1 and the replacement of fluoranthene by C_6D_6 was completed in 30 h (data from ^1H and ^2H NMR spectroscopy and TLC).

In isomeric fluoranthene complexes, η^6, η^6 -IHR were observed in melts for the first times, *i.e.*, the rearrangements proceed in the absence of solvating interactions with solvent molecules, which can lead to elimination of the tricarbonylchromium group from the ligand. Thus when melted in a tube at 154 °C, the complex **38** was completely converted into the isomer **37**, which was established by TLC and NMR spectroscopy. This fact is yet further evidence of the intramolecular character of η^6, η^6 -IHR in tricarbonylchromium complexes of polycyclic aromatic compounds.

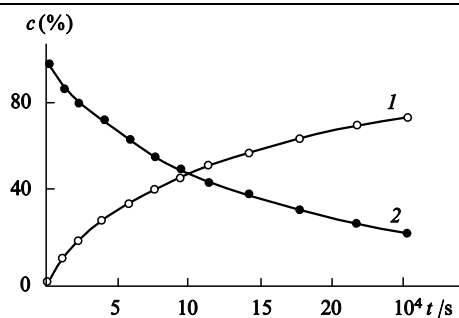


Figure 4. Kinetic curves for changes in the concentration (c) of the complexes **37** (**1**) and **38** (**2**) in the course of IHR.

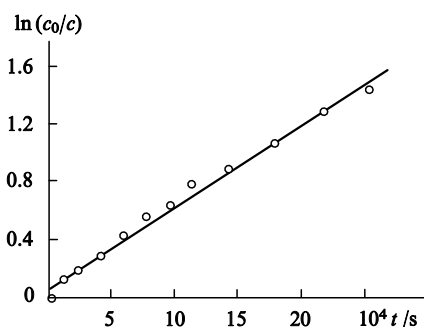
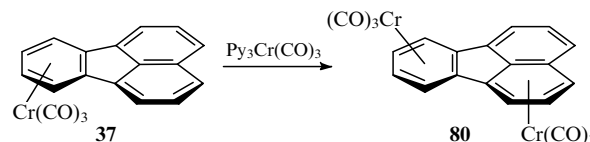


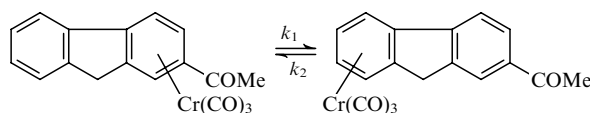
Figure 5. Kinetic first-order dependence for irreversible IHR $38 \rightleftharpoons 37$ at 90 °C; c_0 and c (%) are the initial concentration of the complex **38** and the concentration at time t , respectively.

The rearrangements in fluoranthene complexes proceed substantially more readily than those in biphenyl derivatives for two reasons. First, the ligands in the complexes **37** and **38** are planar (according to the X-ray diffraction data). Second, the difference in thermodynamic stability of the complexes **37** and **38** is substantially larger than that in the case of analogous biphenyl pairs.

The Öfele reaction of the complex **37** with an excess of $\text{Py}_3\text{Cr}(\text{CO})_3$ afforded a binuclear fluoranthene complex (**80**) in 70% yield. The complex **80** has, apparently, a *trans*-structure. It should be noted that the complex **38** did not react with $\text{Py}_3\text{Cr}(\text{CO})_3$ under the same conditions.



Recently, η^6, η^6 -IHR in tricarbonylchromium complexes of 2-acetylfluorene, which is a planar analogue of biphenyl, have been studied by ^1H NMR spectroscopy (deuteriotoluene, 120 °C).¹³⁸



Under these conditions, the intramolecular inter-ring haptotropic rearrangement was accompanied by the replacement of the fluorenyl ligands by deuteriotoluene ($k_{\text{sub}} = 0.19 \times 10^{-5} \text{ s}^{-1}$). According to the kinetic and thermodynamic data [$k_1 = 0.18 \times 10^{-5} \text{ s}^{-1}$, $k_2 = 0.024 \times 10^{-5} \text{ s}^{-1}$, $\Delta G^\ddagger = 33.5 \text{ kcal mol}^{-1}$], the η^6, η^6 -rearrangements in these complexes proceed much more rapidly than those in biphenyl complexes because the ligand in the former complexes (as in the complexes **37** and **38**) is planar.

Therefore, IHR in tricarbonylchromium complexes with different polycyclic aromatic ligands have been studied in sufficient detail. The kinetic and thermodynamic parameters of these rearrangements, which depend on the structure of the ligand and the nature of the substituents, are summarised in Table 8. The

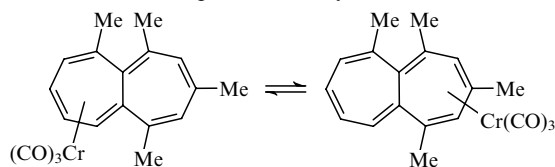
Table 8. Kinetic and thermodynamic data for η^6, η^6 -IHP in tricarbonylchromium complexes with polycyclic ligands.

Ligand	T/K	K_{eq}	$10^5 k_1^a$ / s^{-1}	$\Delta G^\ddagger$ / kcal mol^{-1}	E_a^b / kcal mol^{-1}
2-Methyl-naphthalene	358	2.09	3.02	28.5	26.9
Methylace-naphthene ^c	363	1.13	1.00	29.7	27.5–26.8
Fluoranthene	363	(see ^d)	0.73	30.0	27.8–28.1
Methylace-naphthylene	363	1.18	2.29	29.1	26.9–25.5
1-Deuteriobiphenylene	393	1.00	4.79	31.0	28.6–27.8
4-Deuteriobiphenyl	447	1.00	6.42	35.1	32.4–31.5
4-Bromobiphenyl	447	(see ^d)	5.13	35.3	32.6–31.72
2-Bromobiphenyl	447	(see ^d)	2.23	36.04	32.5–33.4

^a The rate constant k_1 defines the rate of migration of the tricarbonylchromium group between the substituted and unsubstituted rings. ^b The value was calculated taking into account average $\Delta S^\ddagger$. ^c Data for the *exo*-complexes. ^d Irreversible IHR.

data on IHR in complexes of other transition metals with polyaromatic ligands are scarce. Nevertheless, these data indicate that the rates of rearrangements depend substantially on the nature of transition metal and the ligand environment.

In conclusion, note that the first example of η^6, η^6 -IHR in fused nonplanar polycycles, *viz.*, in tricarbonylchromium complexes of substituted heptalene, which occur under rather drastic conditions, has been reported recently.¹³⁹



6. Theoretical approach to studies of inter-ring haptotropic rearrangements in transition metal complexes with polycyclic aromatic ligands

During the progress of experimental investigations of IHR it became evident that further advances in studies of these processes could not be achieved without application of quantum-chemical methods. At present, *ab initio* high-level quantum-chemical calculations for heteroorganic and organometallic compounds are complicated. The restricted Hartree–Fock–Roothaan method with the use of small basis sets is well suited to studies of organic molecules. However, this method is inefficient in investigations of organometallic compounds. In the latter cases, it is necessary to perform calculations using larger basis sets with polarisation functions taking into account electronic correlations and relativistic corrections. As a result, theoretical studies were generally performed using semiempirical methods for calculating the structures and properties of organometallic compounds and only qualitative results were obtained. Recently, the application of the DFT method has opened prospects for obtaining reliable quantitative data.

Theoretical studies of the mechanisms and the major regularities of IHR in different systems were surveyed in a review.¹⁴⁰ The pioneering investigations in this field were carried out by Albright *et al.*⁴⁷

7. Studies of the mechanism of η^6, η^6 -haptotropic rearrangements in naphthalenechromium tricarbonyls by the density functional method

Recently, it has been demonstrated that time-saving calculations by the DFT method can give high-quality data competitive with the results of *ab initio* high-level quantum-chemical calculations.¹⁴¹ The fact that the kinetic parameters of IHP in naphthalene complexes are weakly sensitive to the effect of the substituents in the ligand is somewhat unexpected (see Table 6) because the effects of the substituents are pronounced in the majority of other metallotropic rearrangements. Detailed investigations of the mechanism of the rearrangements by the DFT method provided reasonable explanations for this fact. Calculations were carried out with the use of the most-time-saving program with extended basis sets.¹⁴¹ The results reproduced adequately the geometric parameters of tricarbonyl(η^6 -naphthalene)chromium (**4**) determined by X-ray diffraction analysis,⁸⁵ including such details as the differences between the Cr–C(1) and Cr–C(2) bond lengths and between the Cr–C(4a) and Cr–C(8a) bond lengths (see the note in Table 9).

The results of calculations are given in Tables 9 and 10. These results agree qualitatively with the results obtained in another study.⁴⁷ In particular, migration of the Cr(CO)₃ group from one ring to another along the shortest path through the midpoint of the C(4a)–C(8a) bond is forbidden in the case of the basis states **A** and **B**.

Table 9. Comparison of the calculated geometric parameters of the model molecules with the experimental data.

Bond	Calculated values /Å	Experimental values /Å	Deviation ^a
Cr(CO) ₆ (see ^b)			
Cr–C	1.908	1.924	–0.016
C–O	1.153	1.165	–0.012
(η^6 -C ₆ H ₆)Cr(CO) ₃ (see ^c)			
Cr–C _{CO}	1.846	1.863	–0.017
Cr–C _{PhH}	2.222	2.208	0.014
C–C	1.410, 1.426	1.417	0.001
(η^6 -C ₁₀ H ₈)Cr(CO) ₃ (see ^d)			
Cr–C _{CO}	1.847	1.815–1.830	0.025
Cr–C(1)	2.218	2.186, 2.214	0.018
Cr–C(2)	2.214	2.213, 2.214	0.001
Cr–C(4a)	2.336	2.306, 2.337	0.015
C(2)–C(3)	1.426	1.375	0.051
C(3)–C(4)	1.405	1.389, 1.383	0.019
C(4)–C(4a)	1.439	1.447, 1.404	0.014
C(4a)–C(8a)	1.442	1.439	0.003

Note. The atomic numbering scheme used for (η^6 -C₁₀H₈)Cr(CO)₃ is shown in Scheme 1.

^a The difference between the experimental and calculated values. ^b The experimental values were determined by electron diffraction study.¹⁴²

^c The experimental values were determined by electron diffraction study.¹⁴³ ^d The experimental values were determined by X-ray diffraction analysis.⁸⁵

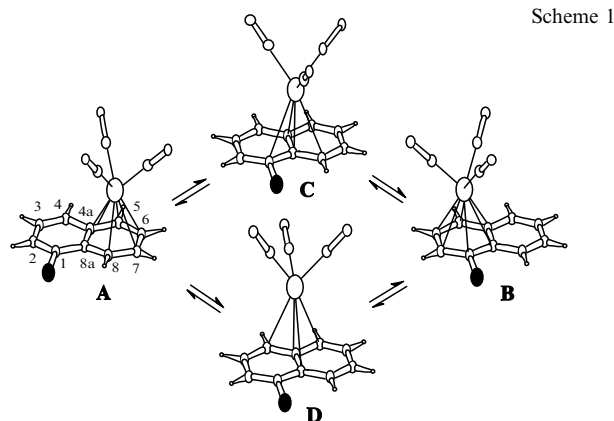


Table 10. Relative energies of the isomeric complexes **A** and **B** and the transition states **C** and **D** (kcal mol^{–1}).

R	A	B	C	D
H	0	0	30.44	30.44
1-Cl	0	2.78	33.93	30.82
2-Cl	0	2.22	30.23	30.91
1-SiMe ₃	–1.64	0	29.59	30.63
2-SiMe ₃	–4.47	0	26.41	26.62
1-Me	0.52	0	32.18	30.38
2-Me	–0.19	0	28.86	29.92

The transition state for (η^6 -C₁₀H₈)Cr(CO)₃ (**3**) has the structure of the trimethylenemethane complex with the symmetry C_{2v} in which the Cr(CO)₃ group is coordinated through the C(4), C(4a), C(5) and C(8a) atoms and is slightly shifted to the periphery of the ligand. The potential energy surface does not have a stationary point (a local minimum) corresponding to an inter-

mediate of the η^3 -allylic type, which had been postulated in another study.⁴⁷

For tricarbonylchromium complexes of substituted naphthalenes, the tricarbonylchromium group can migrate between the substituted and unsubstituted rings *via* two paths through the transition states **C** and **D**. The results of calculations reproduce adequately the relative stabilities of the isomers **A** and **B**, which differ by the position of the $\text{Cr}(\text{CO})_3$ group in the unsymmetrically substituted naphthalene ligand. The presence of the substituent changes the energy of the transition state **C** in which this substituent is located in the immediate vicinity of the migrating group, whereas the energy of the transition state **D** changes only slightly ($\pm 0.5 \text{ kcal mol}^{-1}$). Therefore, the existence of two reaction pathways one of which is virtually undisturbed is, on the whole, responsible for the low sensitivity of the kinetic parameters of the rearrangement to the effects of the substituent in the ligand. Taking into account the assumptions made (the isolated-molecule approximation was used and the difference in the zero-point energy was ignored), the calculated activation barriers agree well with the experimental $\Delta G^\ddagger$ values.

IV. Conclusion

Essentially all known data on IHR in π -complexes of transition metals with fused polycyclic ligands are surveyed in the present review. Metallotropic rearrangements revealed in new complexes and elucidation of the general regularities of these rearrangements are of considerable importance because they gave impetus to the development of new synthetic procedures.

Presently, the general concepts of IHR are rather clearly stated. Further studies should be aimed at the more detailed theoretical description of these processes, in particular, it is necessary to have an idea of the structures of transition states in the course of IHR to perform the directed construction of new tautomeric systems. In this respect, calculations of the potential energy surfaces for the rearrangements with the use of more rigorous quantum-mechanical methods will be of paramount importance.

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Fluoroindate glasses

P P Fedorov, R M Zakalyukin, L N Ignat'eva, V M Bouznik

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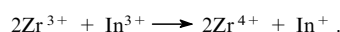
Abstract. The compositions, properties and concepts of the structure of fluoroindate glasses are considered. These glasses are characterised by low phonon energies and hence very low theoretical optical losses in the IR region. According to the vibrational spectroscopic data, the degree of polymerisation of octahedra in fluoroindate glasses is lower than in fluorogallate and fluoroaluminate glasses. The compositions of fluoroindate glasses containing up to nine components cannot be regarded as being completely optimised. Comparative analysis of the chemical and thermal stability of fluoroindate and fluorozirconate glasses was performed. It is shown that the high susceptibility of indium fluoride to hydrolysis accounts for the instability of glasses and optical losses. The prospects for the use of fluoroindate glasses in lasers, fibre optics and scintillation instruments are discussed. The bibliography includes 157 references.

I. Introduction

Intensive studies of fluoride glasses began in the mid-1970s. At that time, fluoroberyllate and fluoroaluminate glasses were well known. An unexpected discovery of fluorozirconate glasses with high values of coordination numbers (c.n.) of glass-forming atoms (c.n. 6–8) stimulated the development of studies of glass formation in multicomponent fluoride systems and revealed other fluorides as 'progenitors of glass'. Fluoride glasses are promising optical materials, including their prospective use in telecommunication systems, because they are characterised by a much wider

transmission region in the IR range compared to silicate glasses. Various experimental and computational methods are employed in the studies of the structure of fluoride glasses. Experimental results are described using different models of glassy state (crystal, disordered network, stressed mixed clusters, chemical twinning, ionic glass, polymeric, colloidal, *etc.*). A number of criteria of glass formation have been proposed.^{1–11}

At present, the best studied glasses are based on zirconium fluoride of the type ZBLAN (53 ZrF₄ · 20 BaF₂ · 4 LaF₃ · 3 AlF₃ · 20 NaF).[†] In order to prevent reduction of Zr⁴⁺ to Zr³⁺, the fluorozirconate glasses of ZBLAN type are doped with small amounts of indium fluoride (0.015 mol.% – 0.25 mol.%).^{12, 13} In this case, no reduction occurs because the couple In³⁺/In⁺ (like, *e.g.*, Sn⁴⁺/Sn²⁺ but not Ga³⁺/Ga⁺) has a larger electrochemical potential than the couple Zr⁴⁺/Zr³⁺ (see Refs 14 and 15). The following redox reaction takes place



An analogous role seems to be played by the additive InF₃ to fluorohafnate glasses: they prevent reduction of Hf⁴⁺ to Hf³⁺.^{16–18} The presence of univalent indium in the glass leads to the appearance of a double absorption peak in the UV region.¹⁴

Upon addition of up to 4 mol.% of InF₃ to ZBLAN, the resistance of this glass to crystallisation is slightly increased. The refractive index is also increased but less essentially than upon addition of PbF₂.¹⁹ Upon addition of up to 3 mol.% of InF₃ to the fluorozirconate glass of ZBLALi type with a high (~ 8 mol.%) content of PbF₂, no stabilisation effect was achieved.²⁰ The increase in the InF₃ concentration in the fluorohafnate glass containing 5 mol.% of CeF₃ induced a decrease in the integral yield of Ce³⁺ luminescence.¹⁸ Attempts to stabilise the glass with composition 24 CdF₂ · 29 CdCl₂ · 11 BaF₂ · 36 NaF by adding up to 8 mol.% of InF₃ were unsuccessful.²¹

In recent years, investigators have shown an appreciable interest in glasses with high content of indium fluoride, the so-called fluoroindate glasses. These glasses are characterised by lower mean values of the energy of phonons (~ 510 cm⁻¹) than conventional fluorozirconate glasses (~ 580 cm⁻¹).²² Thus, fluoroindate glasses absorb in a farther IR region. The range of transparency extends from the UV region to ~ 7–8 μm in the IR region (for fluorozirconate and fluoroaluminate glasses, this extends from the UV region to ~ 5.5 μm).[‡] Consequently, the

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[†] Hereinafter, the compositions of glasses are given in mol.%.

[‡] The edges of transparency are determined approximately, since they depend not only on the sample composition, but also on its thickness.

calculated values of minimum optical losses determined by the sum of the Rayleigh scattering and the multiphonon absorption are substantially smaller in fluoroindate glasses than in fluorozirconate glasses. For example, for the glass BIZYbT (30 BaF₂ · 30 InF₃ · 20 ZnF₂ · 10 YbF₃ · 10 ThF₄) such losses reach ~ 0.002 dB km⁻¹ at a wavelength of 3 μm,²³ while for ZBLAN they are ~ 0.044 dB km⁻¹ at a wavelength of 2.55 μm.²⁴ Therefore, fluoroindate glasses may be regarded as promising materials for the IR instrumentation, in particular in systems of optical fibre communication for the transmission of information in the IR region. However, because of technological difficulties the real optical losses are far from the calculated values: they are larger than in the ZBLAN-based fibres and still larger than in the silicate optical fibres (see below). We are still far from the time when it will be possible to use the calculated characteristics of fluoroindate glasses for the development of many-kilometre fibre optical systems for the transmission of information in the range of 2.5–3.7 μm. Characteristically, the impurities of 3d elements which affect the transmittance in fluoride glasses in the 0.7–1.5 μm range, even if present in negligible amounts, have virtually no effect on the transmission in the 2.5–3.2-μm range. In the latter range, an essential contribution to the absorption is made by the OH groups (the band at 2.9 μm),^{24–26} which creates technological difficulties because of easy hydrolysis of indium fluoride. Other anionic impurities, in particular SO₄²⁻, also influence essentially optical characteristics of fluoroindate glasses in this range.²⁷

The prospects for the use of fluoroindate glasses in the communication optical fibre systems is related to specific features of real silicate fibre-based systems with losses below 1 dB km⁻¹. In the first-generation systems known since 1976, use is made of multi-mode fibres (the operating wavelength is 0.8 μm). Systems of the next generation developed in 1983 are based on the use of both single- and multi-mode fibres (the operating wavelength is 1.3 μm, the second telecommunication window). Modern third-generation systems operate at the wavelength 1.5 μm (the third communication window), which corresponds to the minimum optical losses of the silicate fibre.²⁸ The systems of all the three generations require installation of laser amplifiers of the signal at intervals of a few tens of kilometres.

The fluoride glasses and especially the fluoroindate glasses are characterised by low energies of phonons; therefore, they can be used as a base for the design of efficient lasers with high quantum yield (up to 6%–7%).²⁹ For different operating wavelengths, glasses are doped with ions of rare-earth elements, *viz.*, with Tm³⁺, 0.8 μm; Pr³⁺ or Nd³⁺, 1.3 μm; Er³⁺, 1.5 μm (Ref. 30). Doping of fluoroindate glasses with ions of rare-earth elements is easier than that of fluorozirconate glasses.³¹ In recent years, the subject of most active development is the fluoride fibre doped with Pr³⁺ ions, which is required for the design of optical amplifiers used in telecommunication systems.^{17, 32, 33}

The active element of fibre communication is the optical fibre composed of the core and the cladding. A number of requirements are set for the respective materials. The refractive index of the core (*n*₁) should be larger than that of the cladding (*n*₂), while the coefficients of thermal expansion and the temperatures of glass transition and crystallisation of the core and the cladding should be close. In order to achieve the maximum operation efficiency of laser amplifiers, it is necessary to use single-mode optical fibres (*i.e.*, fibres with a small diameter of the core ranging from 3 to 5 μm) with a large (0.35–0.4) aperture.^{20, 34}

$$N_A = (n_1^2 - n_2^2)^{1/2}$$

or the quantity

$$\Delta n = \frac{n_1 - n_2}{n_1}.$$

It is possible that fluoroindate glasses will also find application as optical waveguides (in particular in medicine) for the transmission of laser radiation in the IR region from Er:YAG solid

(2.94 μm) and CO gas (4.8–5.5 μm) lasers. The limiting factor is the threshold of glass damage.²⁹

Chalcogenide (of the As₂S₃ type) and chalcogen halide glasses [*e.g.*, formed in the Ge–As–Te–I and Hg–Pb–SI systems,³⁵ as well as halide (*e.g.*, bromide³⁶ and mixed chloride-fluoride²¹)] glasses are characterised by lower mean energies of phonons than fluoroindate glasses. Chalcogenide glasses are transparent much farther into the IR region; however, their transmission in the visible spectral region is limited. Mixed halide glasses are unstable in the ordinary atmosphere and undergo easy hydrolysis.

Compared to the fluorozirconate glasses, the fluoroindate glasses possess enhanced thermal stability judging from the difference in glass transition temperatures (*T*_g) and the onset of exothermic of crystallisation (*T*_x) on the heating curves

$$\Delta T = T_x - T_g$$

or from the Hruby criterion³⁷

$$H = \frac{T_x - T_g}{T_m - T_x},$$

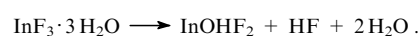
where *T*_m is the melting temperature.[§]

In the opinion of some investigators (see, *e.g.*, Ref. 39), the fluoroindate glasses are more stable than the fluorozirconate ones. The preparation of bulk castings of fluoroindate glasses requires lower cooling rates of glass-forming melts.⁴⁰ Apparently, this characteristic depends strongly on the technology of preparation of glasses (oxygen-containing impurities induce their crystallisation).⁴¹

The critical cooling rates (*R*_c) of glass-forming melts can be determined experimentally (*e.g.*, by the method proposed by Barandiaran and Colmenero⁴²), *viz.*, from the dependences of the observed supercooling Δ*T*₁ (the difference between the temperatures of liquidus and the beginning of crystallisation) on the cooling rate *R* (linear extrapolation to the infinite supercooling using ln*R*–1/Δ*T*₁² coordinates). Yet another method consists in calculations using the data derived from the TTT (temperature–time–transformation) curves.^{43, 44} Both methods require laborious experiments. The values of *R*_c reported from different studies show strong discrepancies. Thus the *R*_c values measured by the former method for the five-component glass (30 BaF₂ · 30 InF₃ · 20 ZnF₂ · 10 YbF₃ · 10 ThF₄) differ by nearly two orders of magnitude: 1.7 K min⁻¹ (Ref. 45) and 120 K min⁻¹ (Ref. 44) (for ZBLAN, these values were 0.7 and 3 K min⁻¹, respectively). Measurements by the last-mentioned method gave *R*_c = 102 K min⁻¹ (for ZBLAN, this value was 8 K min⁻¹).²³ Such a difference is possibly explained by different conditions of preparation of the samples.

II. Physicochemical properties of indium fluoride

At normal pressure, indium fluoride has the high-temperature cubic polymorph of the ReO₃ type.⁴⁶ As the temperature decreases, it passes into the trigonal polymorph of the VF₃ type, space group *R* $\bar{3}c$ (Fig. 1). The melting temperature of InF₃ is 1320 °C.^{48, 49} Indium fluoride is characterised by high vapour pressure,⁵⁰ it vaporises strongly upon heating above 900 °C, undergoes easy hydrolysis upon slight heating and absorbs moisture when stored in air. Its hydrate InF₃ · 3H₂O can hardly be dehydrated because its hydrolysis with water of crystallisation occurs even at room temperature⁵¹



The ionic radius of In³⁺ is substantially smaller than those of lanthanide cations, it is close to the radius of scandium ion and is

§ In the original paper,³⁷ the temperature of the beginning of melting (solidus) is used in this formula; in a number of other papers (see, *e.g.*, Ref. 38) the temperature of liquidus is used. The difference between them may be substantial.

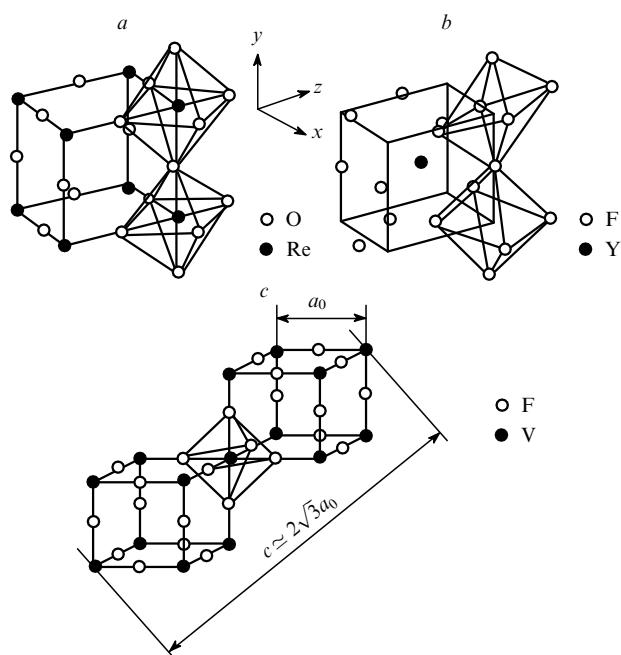


Figure 1. Structural types ReO_3 (a), $\beta\text{-YF}_3$ (b)⁴⁷ and VF_3 (c).

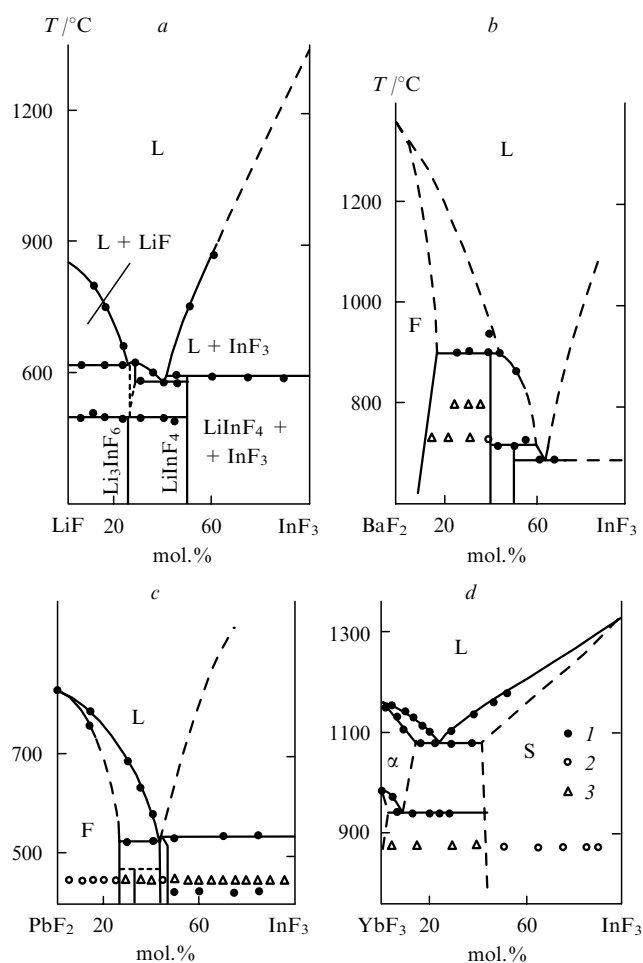


Figure 2. Phase diagrams of the systems $\text{LiF}-\text{InF}_3$ (a), $\text{BaF}_2-\text{InF}_3$ (b), $\text{PbF}_2-\text{InF}_3$ (c) and $\text{YbF}_3-\text{InF}_3$ (d).^{48,53} (1) DTA data; (2) single-phase samples; (3) two-phase samples from X-ray powder diffraction data; L, melt; F, solid solution with the fluorite structure; S, solid solution with the ReO_3 structure; α , solid solution with the $\alpha\text{-YF}_3$ structure.

substantially larger than the radii of gallium and aluminium ions.⁵²

Ion	La^{3+}	Y^{3+}	Lu^{3+}	In^{3+}	Sc^{3+}
$r/\text{\AA}$ (c.n. 8)	1.30	1.159	1.117	1.06	1.01

A morphotropic transition occurs on going from InF_3 to trifluorides of heavy rare-earth elements (Lu–Er, Y). Indium fluoride is partially dissolved in high- and low-temperature RF_3 polymorphs corresponding to the structural types $\alpha\text{-YF}_3$ and $\beta\text{-YF}_3$, respectively.⁵³

Being a strong Lewis acid, indium fluoride forms numerous compounds with fluorides of uni- and divalent metals (Fig. 2).^{46,54}

III. Optimisation of glass compositions

Undoped indium fluoride is not vitrified. However, like other Lewis acids, such as AlF_3 , ZrF_4 , GaF_3 , ZnF_2 (Fig. 3), it is the ‘progenitor’ of glass. According to the proposed classification,¹¹ indium fluoride is classed as a glass former of second degree, since at ordinary quenching rates ($\sim 10^3 \text{ K s}^{-1}$) glasses are formed in some binary systems, namely, $\text{InF}_3-\text{BaF}_2$,^{55,56} $\text{InF}_3-\text{PbF}_2$ ⁵⁷ and $\text{InF}_3-\text{SrF}_2$.⁵⁸ The regions of glass formation in the first two systems are in the vicinity of eutectic points; the phase diagram of the third system has not been studied.

First reports on the synthesis of fluorindate glasses appeared in the early 1980s.^{55,59} A double glass-forming system $\text{BaF}_2-\text{InF}_3$ was found;⁵⁵ however, the glass formed in this system was not sufficiently stable. Numerous stabilising components, viz., YF_3 , UF_4 ,⁵⁵ FeF_3 ,⁶⁰ ZnF_2 , ThF_4 ,⁶¹ YbF_3 ,^{23,55,62} ScF_3 , GaF_3 , CdF_2 ,⁶³ SrF_2 ,⁵⁸ MgF_2 ,^{57,64} BiF_3 ⁶⁵ and $\text{In}(\text{PO}_3)_3$,⁶⁶ were proposed. A second glass-forming system $\text{PbF}_2-\text{InF}_3$ was found almost simultaneously which was doped with CdF_2 , ZnF_2 , MnF_2 and SnF_2 as stabilising ingredients.

The regions of glass formation in some ternary systems are shown in Fig. 4. Note that the boundaries of the regions of glass formation are tentative. These depend on the experimental conditions and are in particular very strongly dependent on the cooling rate. The data from different studies on the regions of glass formation correlate but do not coincide. For example, glass formation was observed in the binary system $\text{BaF}_2-\text{InF}_3$,^{55,61} whereas according to the results of another study,⁶³ only three-component systems $\text{BaF}_2-\text{InF}_3-\text{MF}_n$ did undergo vitrification. The results of studies on the system $\text{BaF}_2-\text{InF}_3-\text{YF}_3$ (cf. Refs 57 and 61) are at variance [two regions of glass formation were revealed (cf. Ref. 57, Fig. 4b)]. It was stated that the system $\text{BaF}_2-\text{InF}_3-\text{GaF}_3$ has an isolated region of glass formation,⁶³ while Boutarfaia *et al.*⁵⁷ revealed a ‘belt’ region between the systems $\text{BaF}_2-\text{InF}_3$ and $\text{BaF}_2-\text{GaF}_3$ (see Fig. 4d). Some discrepancies are found even within the framework of a single study. In particular, in a study,⁶⁰ of all the studied systems $\text{PbF}_2-\text{InF}_3-\text{MF}_n$ the glass formation in a binary system $\text{PbF}_2-\text{InF}_3$ was revealed only in a single case (see Fig. 4g), while in other cases the glass formation was observed only in three-component systems (Fig. 4h,i).

In three-component systems, the rate of devitrification is great. Only in the system $\text{PbF}_2-\text{BaF}_2-\text{InF}_3$ was a glass which has prospects for practical application found. Videau *et al.*⁵⁵ have described the four-component glass $40 \text{ InF}_3 \cdot 32 \text{ BaF}_2 \cdot 17 \text{ YF}_3 \cdot 11 \text{ PbF}_2$. A 2 mm-thick sample of this glass had the optical transmission edge of $13 \mu\text{m}$. Auriault *et al.*⁶⁰ obtained a bulk casting for the glass $30 \text{ PbF}_2 \cdot 20 \text{ BaF}_2 \cdot 50 \text{ InF}_3$, the transmission edge in the IR region being $\sim 8.2 \mu\text{m}$ for a 3 mm-thick sample. Attempts were undertaken to vary the composition of this glass by doping it with ZnF_2 , SrF_2 , AlF_3 , YF_3 , CdF_2 and PbF_2 to enhance stabilisation. Optical characteristics of some 5–8-component glasses (the refractive indices being in the range from 1.549 to 1.566, the edges of IR transmission varying from 7.7 to 8.9 μm) were determined. The possibility of replacement of InF_3 by GaF_3 as well as doping of glasses with rare-earth fluorides were also

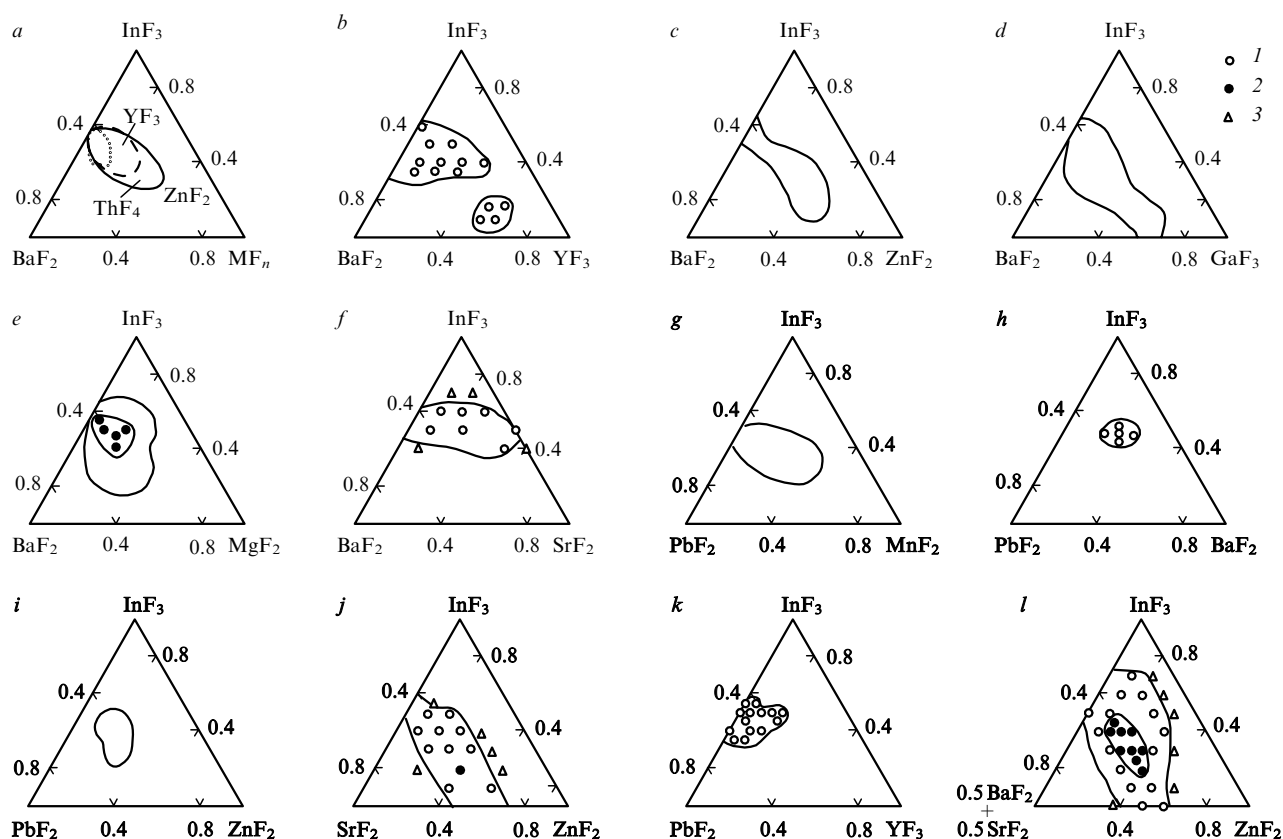


Figure 4. Regions of glass formation in systems involving InF_3 : (a) $\text{BaF}_2\text{--InF}_3\text{--MF}_n$ ($M = \text{Y, Th, Zn}$);⁶¹ (b) $\text{BaF}_2\text{--InF}_3\text{--YF}_3$;⁵⁷ (c) $\text{BaF}_2\text{--InF}_3\text{--ZnF}_2$;⁵⁸ (d) $\text{BaF}_2\text{--InF}_3\text{--GaF}_3$;⁵⁷ (e) $\text{BaF}_2\text{--InF}_3\text{--MgF}_2$;⁵⁷ (f) $\text{BaF}_2\text{--InF}_3\text{--SrF}_2$;⁵⁸ (g) $\text{PbF}_2\text{--InF}_3\text{--MnF}_2$;^{59, 60} (h) $\text{PbF}_2\text{--InF}_3\text{--BaF}_2$;⁶⁰ (i) $\text{PbF}_2\text{--InF}_3\text{--ZnF}_2$;⁶⁰ (j) $\text{SrF}_2\text{--InF}_3\text{--ZnF}_2$;⁵⁸ (k) $\text{PbF}_2\text{--InF}_3\text{--YF}_3$;⁵⁷ (l) $(0.5 \text{ BaF}_2 + 0.5 \text{ SrF}_2)\text{--InF}_3\text{--ZnF}_2$;⁵⁸ (1) quenched glasses; (2) cast glasses; (3) glass-ceramic.

metals) below 10 mol.%. The modified glass IZBS with composition $12.5 \text{ BaF}_2 \cdot 30 \text{ InF}_3 \cdot 30 \text{ ZnF}_2 \cdot 12.5 \text{ SrF}_2 \cdot 8 \text{ NaF} \cdot 5 \text{ CdF}_2 \cdot 2 \text{ LaF}_3$ ⁵⁸ was taken as the base. It turned out that upon substitution of zinc for indium the stability of the glass is decreased. The problem of stability was solved in part by replacement of certain portion of InF_3 by GaF_3 and optimisation of the content of modifiers.

Qui *et al.*⁷⁶ studied the possibility of incorporation of SnF_2 into a glass of the IZBS type with composition $15 \text{ BaF}_2 \cdot 40 \text{ InF}_3 \cdot 20 \text{ ZnF}_2 \cdot 20 \text{ SrF}_2 \cdot 2 \text{ NaF} \cdot 3 \text{ GdF}_3$. It was found that it is possible to replace BaF_2 , ZnF_2 or SrF_2 by SnF_2 (up to 15 mol.-%–20 mol.-%); however, in all the cases T_g and the difference $T_x - T_g$ decreased. With the SnF_2 content above 20 mol.%, crystal phases appear, including that of InF_3 . Upon variation of the BaF_2 to SrF_2 ratio, a glass with intermediate composition was selected which exhibited maximum stability (judging from the ΔT value).

Zhang and Poulain³¹ studied the effect of additions of rare-earth fluorides on the properties of the glass with composition $30 \text{ PbF}_2 \cdot 20 \text{ GaF}_3 \cdot 15 \text{ InF}_3 \cdot 20 \text{ GdF}_2 \cdot 15 \text{ ZnF}_2$; up to 10 mol.% of RF_3 ($R = \text{La, Ce, Pr, Nd, Gd, Er, Yb}$ and Lu) was introduced. It was established that the stability of the glass first increased and then diminished passing through a maximum with 1 mol.-%–2 mol.-% of RF_3 . On the whole, rare-earth fluorides act as modifiers. Up to 20 mol.% of GdF_3 may be incorporated into the glass-forming system $\text{BaF}_2 \cdot \text{InF}_3 \cdot \text{ZnF}_2$;⁷⁷ however, the compositions including 10 mol.% of GdF_3 and 10 mol.% of SrF_2 are the most stable.

Akella *et al.*⁷⁸ studied the possibility of variation of the composition of the nine-component glass $28 \text{ InF}_3 \cdot 20 \text{ ZnF}_2 \cdot 16.5 \text{ BaF}_2 \cdot 12 \text{ GaF}_3 \cdot 9 \text{ PbF}_2 \cdot 6 \text{ NaCl} \cdot 5 \text{ SrF}_2 \cdot 3 \text{ CaF}_2 \cdot 0.5 \text{ PrF}_3$, which has the optical transmission edge at 10 μm . Sodium

chloride was introduced to increase the cross-section of absorption at $f\text{--}f$ transitions of rare-earth elements. It was found that 10 mol.% of GaF_3 can be replaced by InF_3 , 4 mol.% of GaF_3 can be replaced by YF_3 , whereas PbF_2 can be totally replaced by CaF_2 or partially replaced by SrF_2 or BaF_2 without crystallisation.

Delben *et al.*⁷⁹ studied a glass of the type IZBS doped with 5 mol.% of NaCl or LiCl . Complex temperature dependence of viscosity was established and bifurcation of temperature T_g was noted. Taking this into account, a two-phase model of glass was proposed.

Compositions and properties of some fluoroindate glasses are listed in Table 1, while the evolution of their compositions is reflected by Scheme 1.

The stabilities of glasses could be enhanced upon increase in the number of components of the system. This method is known as 'the confusion principle'.⁷⁰ The efficacy of this approach is explained by the fact that it is difficult to attain an ordered structure (the obstruction effect)^{76, 86} with great diversity of types of local ordering, *i.e.*, polymorphism of clusters. It is of note that the glasses BIGaZYbTZr and BIGaZYbTMn ⁶⁹ contain each six (!) glass formers per one modifier. In many cases, the increase in the number of components and isomorphous replacements of one glass component by another result in the appearance of a stabilising 'polycationic effect', which consists in the enhancement of glass stability reaching a maximum for some intermediate composition.⁸⁷ For fluoroindate glasses of different compositions, this effect is observed upon partial isovalent substitution of GaF_3 for InF_3 ^{43, 57, 75, 88} and heterovalent substitution of ZnF_2 for InF_3 ⁷⁵ (isomorphism of glass formers) as well as strontium for barium⁷⁵ (isomorphism of modifiers). Destabilisation observed upon substitution of ZnF_2 for InF_3 is apparently explained by the fact that the initial glass has already been stabilised (the optimum

Table 1. Some properties of fluoroindate glasses: temperatures ($^{\circ}\text{C}$) of glass transition T_g , onset of the exothermic crystallisation T_x , maximum peak of the exothermic crystallisation T_c and onset of melting (solidus) T_m , refractive index for white radiation or at a wavelength of 584.9 nm (n), density ($d/\text{g cm}^{-3}$) and coefficient of thermal expansion ($\alpha/10^7 \text{ K}^{-1}$).

Composition (mol.%)	T_g	T_x	T_c	T_m	n	d	α	Ref.
40 InF ₃ ·43 BaF ₂ ·17 YF ₃	332	400	—	—	—	—	—	55
41 InF ₃ ·43 BaF ₂ ·16 YbF ₃	328	388	—	—	—	—	—	55
40 InF ₃ ·44 BaF ₂ ·16 UF ₄	307	377	—	—	—	—	—	55
40 InF ₃ ·23 BaF ₂ ·21 CaF ₂ ·16 UF ₄	298	357	—	—	—	—	—	55
40 InF ₃ ·32 BaF ₂ ·17 YF ₃ ·11 PbF ₂	304	372	—	—	—	—	—	55
37 InF ₃ ·22 BaF ₂ ·21 MnF ₂ ·15 YF ₃ ·5 LaF ₃	306	356	—	591	—	—	—	80
37 InF ₃ ·22 BaF ₂ ·21 CdF ₂ ·15 YF ₃ ·5 LaF ₃	306	356	—	591	—	—	—	80
20 PbF ₂ ·40 CdF ₂ ·40 InF ₃	222	255	—	—	—	—	—	60
48 PbF ₂ ·25 ZnF ₂ ·27 InF ₃	214	258	—	—	—	—	—	60
40 PbF ₂ ·30 MnF ₂ ·30 InF ₃	209	263	—	—	—	—	—	60
40 PbF ₂ ·25 MnF ₂ ·35 InF ₃	202	238	—	—	—	—	—	60
30 PbF ₂ ·20 BaF ₂ ·50 InF ₃	250	318	—	588	1.5492	—	—	60
20 PbF ₂ ·30 BaF ₂ ·50 InF ₃	283	351	—	—	—	—	—	60
40 BaF ₂ ·40 FeF ₃ ·20 InF ₃	336	409	—	—	—	—	—	60
30 BaF ₂ ·30 InF ₃ ·20 ZnF ₂ ·10 YbF ₃ ·10 ThF ₄	324	447	—	650	1.517	5.56	171	23
50 CdF ₂ ·35 GaF ₃ ·15 InF ₃	285	367	—	580	—	—	—	63
40 InF ₃ ·25 BaF ₂ ·20 ZnF ₂ ·5 CdF ₂ ·10 NaF	283	346	—	537	1.495	5.09	—	63
55 InF ₃ ·22.5 BaF ₂ ·22.5 SrF ₂	324.5	381	386	—	—	—	—	58
40 InF ₃ ·40 BaF ₂ ·20 ZnF ₂	287	360	—	—	—	—	—	58
40 InF ₃ ·20 BaF ₂ ·20 ZnF ₂ ·20 SrF ₂	300.6	388	396	—	1.5005	5.14	187	58
30 InF ₃ ·15 BaF ₂ ·30 ZnF ₂ ·20 SrF ₂ ·5 CdF ₂	290.6	393	401	—	1.4990	5.05	—	81
50 InF ₃ ·40 YF ₃ ·10 BaF ₂	333	416	425	—	—	4.96	—	57
50 InF ₃ ·3 YF ₃ ·33 BaF ₂ ·14 SrF ₂	323	395	401	—	—	5.09	—	57
50 InF ₃ ·5 YF ₃ ·31.5 BaF ₂ ·13.5 SrF ₂	328	412	419	—	—	5.10	—	57
45 InF ₃ ·10 YF ₃ ·31.5 BaF ₂ ·13.5 SrF ₂	339	390	394	—	—	5.07	—	57
45 InF ₃ ·5 YF ₃ ·35 BaF ₂ ·15 SrF ₂	327	385	394	—	—	5.10	—	57
50 InF ₃ ·5 YF ₃ ·13.5 BaF ₂ ·31.5 SrF ₂	332	418	425	—	—	5.02	—	57
40 InF ₃ ·20 BaF ₂ ·20 ZnF ₂ ·20 SrF ₂	300.6	388	396	—	1.5005	5.14	187	58
40 InF ₃ ·20 ZnF ₂ ·20 SrF ₂ ·15 BaF ₂ ·5 CdF ₂	291	383	400	—	1.4980	—	182	39
40 InF ₃ ·20 ZnF ₂ ·5 SrF ₂ ·25 BaF ₂ ·10 PbF ₂	277	366	372	—	1.5300	—	189	39
40 InF ₃ ·20 ZnF ₂ ·20 SrF ₂ ·15 BaF ₂ ·5 CaF ₂	295	385	390	—	—	—	186	39
30 InF ₃ ·30 ZnF ₂ ·20 SrF ₂ ·15 BaF ₂ ·5 NaF	290	380	389	—	1.4870	—	192	39
40 InF ₃ ·20 ZnF ₂ ·20 SrF ₂ ·17 BaF ₂ ·2 GdF ₃ ·LaF ₃	294	390	410	—	1.5080	—	—	39
40 InF ₃ ·20 ZnF ₂ ·20 SrF ₂ ·16 BaF ₂ ·2 GdF ₃ ·2 NaF	290	390	401	—	1.4930	4.99	—	39, 82
15 InF ₃ ·20 GaF ₃ ·30 PbF ₂ ·20 CdF ₂ ·15 ZnF ₂	260	354	364	—	—	—	—	83
	243	354	374	—	1.611	6.017	166	31
30 BaF ₂ ·18 InF ₃ ·12 GaF ₃ ·20 ZnF ₂ ·10 YbF ₃ ·6 ThF ₄ ·4 ZrF ₄	330	442	—	641	1.5050	5.44	171	43
30 BaF ₂ ·18 InF ₃ ·12 GaF ₃ ·16 ZnF ₂ ·10 YbF ₃ ·10 ThF ₄ ·4 MnF ₄	332	442	—	634	1.5090	5.56	—	43
27 BaF ₂ ·18 InF ₃ ·12 GaF ₃ ·20 ZnF ₂ ·10 LuF ₃ ·6 ThF ₄ ·4 ZrF ₄ ·3 PbF ₄	332	478	—	579	—	—	—	26
29 PbF ₂ ·3 PbCl ₂ ·15 InF ₃ ·20 GaF ₃ ·13 ZnF ₂ ·20 CdF ₂	250	370	—	—	1.60	—	170	32
10 BaF ₂ ·61 InF ₃ ·47 ZnF ₂ ·26 SrF ₂ ·4 GaF ₃ ·5 CdF ₂ ·2 LaF ₃	306	380	—	—	1.498	4.88	209	75
15 BaF ₂ ·40 InF ₃ ·20 ZnF ₂ ·20 SrF ₂ ·2 NaF·3 GdF ₃	291	383	—	—	—	5.114	—	76
40 InF ₃ ·20 ZnF ₂ ·20 BaF ₂ ·10 SrF ₂ ·10 GdF ₃	300	405	424	582	—	—	—	77
30 BaF ₂ ·30 InF ₃ ·15 ZnF ₂ ·25 BiF ₃	250	—	350	—	1.578	—	—	65
28 InF ₃ ·20 ZnF ₂ ·16.5 BaF ₂ ·12 GaF ₃ ·9 PbF ₂ ·6 NaCl·5 SrF ₂ ·3 CaF ₂ ·0.5 PrF ₃	—	—	—	—	1.5091	5.15	—	78
36 InF ₃ ·20 ZnF ₂ ·20 SrF ₂ ·16 BaF ₂ ·6 GaF ₃ ·2 NaF	—	—	—	—	1.49	4.8	—	84
30 BaF ₂ ·18 InF ₃ ·12 GaF ₃ ·20 ZnF ₂ ·9 YF ₃ ·6 ThF ₄ ·4 ZrF ₄ ·NdF ₃	320	—	—	—	—	—	—	85
19 ZnF ₂ ·17 InF ₃ ·17 GaF ₃ ·43 PbF ₂ ·4 LaF ₃	236	327	—	460	1.61135	6.32	—	86
30 PbF ₂ ·20 GaF ₃ ·15 InF ₃ ·15 ZnF ₂ ·20 CaF ₂	265	345	—	—	1.564	5.55	—	see ^a

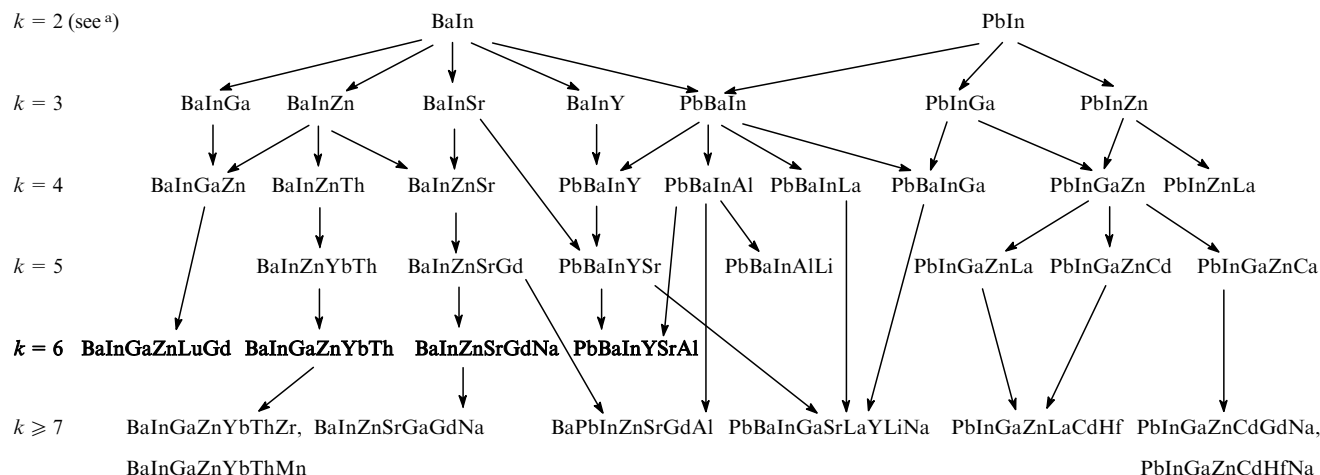
^a The data of R Lebullenger, L A O Nunes and A C Hernandes, in *The XIIth International Symposium on Non-Oxide Glasses and Advanced Materials (Extended Abstracts)*, Florianópolis, Brazil, 2000 p. 439.

ratio InF₃:ZnF₂ has been reached). Upon partial substitution of AlF₃ for InF₃,^{38,43} the stabilities of glasses did not change. Substitutions of SrF₂ for PbF₂ and of PbF₂ for BaF₂ have not been studied systematically. Substitution of PbF₂ for BaF₂ in the BIZYbT glass leads to its destabilisation.⁴³

Considering the isomorphism concept, the substitutions observed are well expected and correspond to the so-called 'geochemical star' of indium.⁸⁹ In particular, a wide heterovalent isomorphism of indium and zinc is known among compounds with different ionicities. From the physicochemical viewpoint and

in conformity with the Rawson principle, the essence of the 'confusion principle' is reduced to the decrease in the temperatures of eutectics as the number of components in the system is increased.¹⁰ It is of note that Bouaggad *et al.*²³ suggested that the five-component composition of BIZYbT with a melting temperature of 650 $^{\circ}\text{C}$ is close to the eutectic composition; however, the thermogram derived from the same study contradicts this suggestion. The thermogram of the IZSB glass does not correspond to the eutectic either.⁹⁰ This discrepancy may be indicative of the potential reserves of the stability enhancement. However, the

Scheme 1



^a k is the number of components; only cationic composition of glasses is indicated.

studies performed so far show that the stabilities of fluoroindate glasses virtually reach 'saturation' with the number of components equal to 6 or 7. The attainment of saturation corresponds to the Bereznoi rule⁹¹ for the temperatures of multicomponent eutectics.

IV. The structures of fluoroindate glasses

In order to elucidate the structures of fluoroindate glasses, it is necessary to know the structures of crystalline compounds which are similar in their compositions to those of the glasses under study and to reveal the types of polymers favouring the glass formation (Stewart's criterion¹). Relevant measurements showed that the temperature dependences of the viscosities of melts of a number of fluoroindate glasses (like those of fluorozirconate glasses) are substantially non-linear in the coordinates $\log \eta \sim 1/T$. This is the indication of 'fragile' glasses and suggests that the polymerisation processes occur during the cooling of melts. This also points to higher ionicities of fluoride glasses compared, *e.g.*, with 'strong' silicate glasses.^{92, 93}

The crystal structures of indium fluoride compounds are very diverse and are similar to the structures of ScF_3 compounds. The indium cation can have c.n. 6 or 7 (it is not ruled out that its c.n. is 8 in solid solutions).

The most characteristic polyhedra are octahedra, often distorted. The structure of InF_3 is a three-dimensional framework of octahedra connected through their vertices (the octahedra are slightly deformed in the low-temperature polymorph). Successive addition of fluorides of uni- and divalent metals to indium fluoride leads to a typical structural depolymerisation of octahedral structures (Fig. 5) with the following sequence: a framework – a layer ($[\text{InF}_4]^-$, compounds MInF_4) or a corrugated layer (LiInF_4) – a framework ($[\text{In}_3\text{F}_{14}]^{5-}$, compounds $\text{M}_3\text{In}_3\text{F}_{14}$ of the chiolite type) – a chain ($[\text{InF}_5]^{2-}$, BaInF_5) – isolated octahedra ($[\text{InF}_6]^{3-}$, compounds M_3InF_6). In all the cases, the octahedra are linked by vertices through the bridging fluorine atoms.^{54, 94, 95}

The structure of high-temperature $\beta\text{-Ba}_3\text{In}_2\text{F}_{12}$ (the structural type $\text{Sr}_3\text{Fe}_2\text{F}_{12}$) comprises chains of octahedra, in addition to isolated octahedra. Ternary compounds with octahedral formations are known (*e.g.*, of the type of weberite $\text{Na}_2\text{M}^{\text{II}}\text{InF}_7$). Compounds with octahedra $[\text{InF}_6]^{3-}$ are isostructural to the corresponding fluoroaluminates and fluorogallates.⁹⁴

Yet another important structural motif, which can give polymeric structures, are seven-vertex pentagonal bipyramids $[\text{InF}_7]^{4-}$. In compounds of the KIn_2F_7 type, such bipyramids bind to each other through equatorial edges, form layers which are in turn linked to form a three-dimensional framework through the vertices of bipyramids. In compounds $\text{M}_2\text{In}_3\text{F}_{11}$ and $\text{MIn}_3\text{F}_{10}$

($\text{M} = \text{K}, \text{Rb}, \text{Cs}$), junctions of bipyramids with octahedra occur. Crystallochemical analysis showed that the structures containing $[\text{InF}_7]^{4-}$ are related to the $\alpha\text{-U}_3\text{O}_8$ structure, which in turn is a derivative of the $\alpha\text{-UO}_3$ structure.⁹⁶ Thus, the corresponding fluoroindates may be regarded as the products of depolymerisation of the virtual InF_3 polymorph of the $\alpha\text{-YF}_3$ ($\alpha\text{-UO}_3$) type. According to the data of X-ray powder diffraction, the structural type inherent in high-temperature polymorphs of fluorides of heavy rare-earth elements is identical to $\alpha\text{-UO}_3$. It may also be described as anti- Li_3N . The structure of hypothetical RF_3 proposed by Aleonard *et al.*⁹⁶ may also be one of the $\alpha\text{-YF}_3$ models. On the basis of the corresponding RF_3 polymorphs, solid solutions with indium fluoride are formed (see Fig. 2). The structures of BaR_2F_8 compounds of the type of ortho-rhombic BaTm_2F_8 ($\text{R} = \text{Dy} - \text{Yb}$) and monoclinic BaLu_2F_8 , in which isomorphous substitutions of indium for rare-earth elements are possible, are related to the structural type $\alpha\text{-YF}_3$.⁹⁷

Yet another type of seven-vertex polyhedron which is found in fluoroindates may be described as trigonal prisms with one capped lateral face. Slightly distorted polyhedra of this type are present in the structures Sr_2InF_7 ⁹⁸ and Pb_2InF_7 , which is isostructural to the former, whereas paired seven-vertex polyhedra linked along the edge are found in the low-temperature polymorph of $\alpha\text{-Ba}_3\text{In}_2\text{F}_{12}$.⁹⁹ Judging from the interpretation of KYF_4 ,¹⁰⁰ which is isostructural to NaInF_4 , the structure of the latter contains chains of the above-mentioned seven-vertex polyhedra. They may be regarded as the products of polymerisation through collectivisation of the 'caps' of dimeric groups identified in $\alpha\text{-Ba}_3\text{In}_2\text{F}_{12}$. The structure of ortho-rhombic polymorphs of $\beta\text{-YF}_3$ (see Fig. 1) in which InF_3 can also be dissolved (see Fig. 2) may also be represented as the result of polymerisation of such polyhedra to form a three-dimensional framework due to which they are transformed into eight-vertex polyhedra by acquiring one more 'cap' (trigonal prisms with two centred faces).

Thus, in fluoroindate (like in fluorozirconate) glasses different structural units can be responsible for glass formation. In conformity with the known diagrams,^{57, 61} the regions of glass formation in the systems $\text{BaF}_2 - \text{InF}_3 - \text{MF}_n$ adjoin the region of primary crystallisation of compound BaInF_5 (see Figs 2, 4), which testifies in favour of the octahedral structures of these glasses.

However, the facts that the system $\text{BaF}_2 - \text{InF}_3 - \text{YF}_n$ contains, in addition to the region of glass formation adjoining the side $\text{BaF}_2 - \text{InF}_3$, yet another region similar in composition to that of BaY_2F_8 ⁵⁷ and that two types of glasses exist with considerably different T_g allow one to suggest the presence of two structural motifs in fluoroindate glasses (octahedra and pentagonal bipyramids). However, this may simply be related to the existence of two eutectics (without structural differentiation). Grande *et al.*¹⁰¹

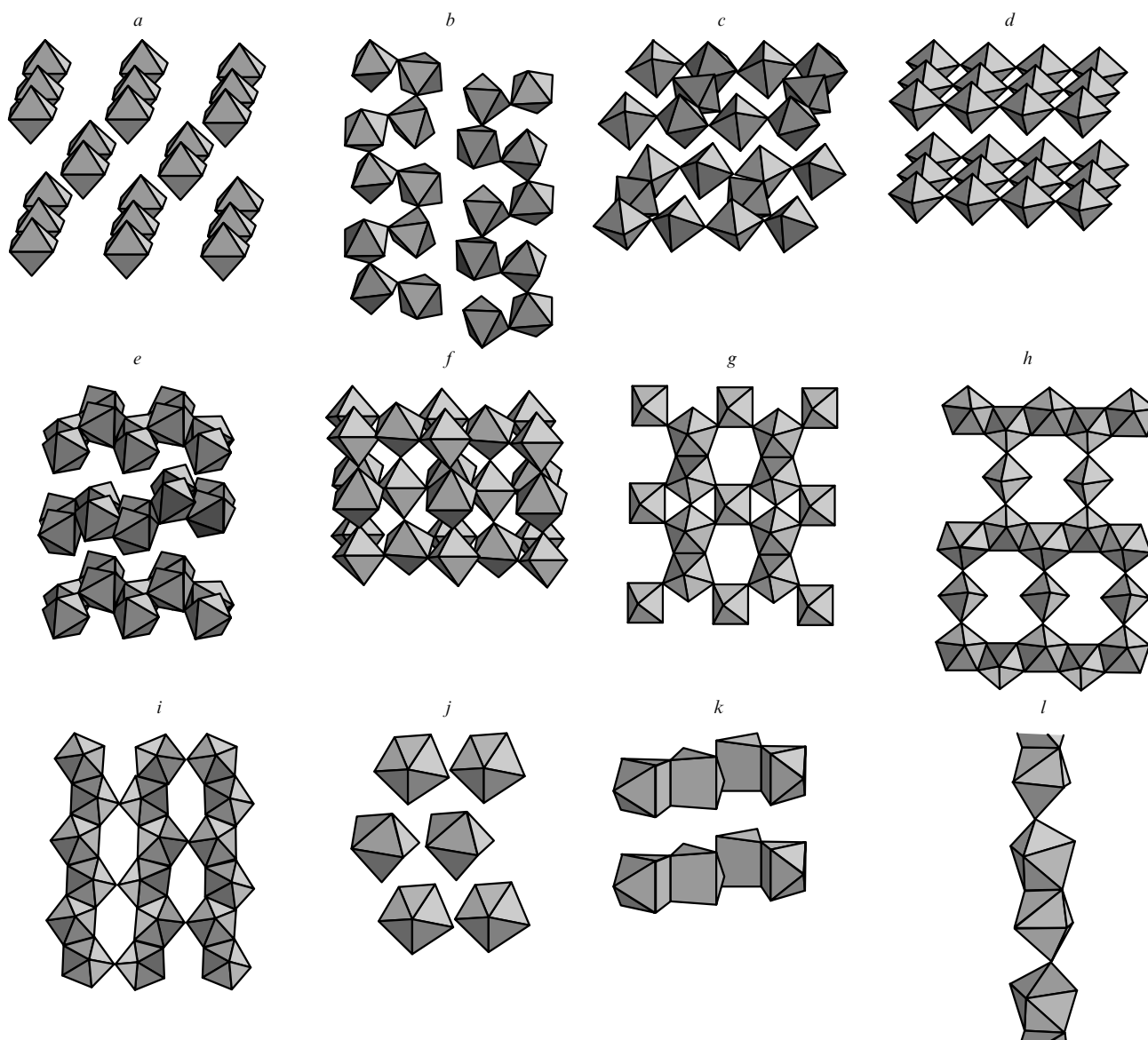


Figure 5. Packings of $[\text{InF}_6]^{3-}$ and $[\text{InF}_7]^{4-}$ polyhedra in structures of fluoroindates: (a) $[\text{InF}_6]^{3-}$ in the M_3InF_6 structure; (b) $[\text{InF}_5]^{2-}$ in the BaInF_5 structure; (c) $[\text{In}_3\text{F}_{14}]^{5-}$ in the $\text{M}_5\text{In}_3\text{F}_{14}$ structure; (d) $[\text{InF}_4]^-$ in the MInF_4 structure; (e) $[\text{InF}_4]^-$ in the LiInF_4 structure; (f) InF_3 ; (g) $[\text{In}_3\text{F}_{10}]^{3-}$ in the $\text{MIn}_3\text{F}_{10}$ structure; (h) $[\text{In}_3\text{F}_{11}]^{2-}$ in the $\text{M}_2\text{In}_3\text{F}_{11}$ structure; (i) $[\text{In}_2\text{F}_7]^-$ in the MIn_2F_7 structure; (j) $[\text{InF}_7]^{4-}$ in the Sr_2InF_7 structure; (k) $[\text{In}_2\text{F}_{12}]^{6-}$ in the structure of low-temperature phase $\text{Ba}_3\text{In}_2\text{F}_{12}$; (l) $[\text{In}_2\text{F}_{11}]^-$ in NaInF_4 .

noted the glass formation on the basis of lithium nitride, which is structurally related to BaY_2F_8 .

Wide isomorphism with Ga in fluoride glasses (*cf.*, *e.g.*, Refs 57, 75, 82) suggests the octahedral surrounding of indium. Isomorphism with aluminium is usually restricted;³⁸ however, complete isomorphism of Al^{3+} and In^{3+} (though, with the conjugated replacement of barium and lead) in both the crystalline and glassy states occurs in the system $\text{PbF}_2\text{--BaF}_2\text{--AlF}_3\text{--InF}_3$.^{41, 102}

Analysis of binary glasses containing 50 mol.%–67 mol.% of InF_3 in combination with BaF_2 or SrF_2 by the EXAFS method showed that the nearest surrounding of indium is octahedral, the distance In--F (2.06–2.07 Å) being virtually the same as in InF_3 (2.05 Å).¹⁰³ According to the data from EXAFS, X-ray radial distribution function and molecular dynamics for the glass $45\text{InF}_3\cdot 40\text{BaF}_2\cdot 15\text{ErF}_3$, the mean c.n. values are 7.15, 8.86 and 7.83 for In, Ba and Er, respectively. According to the X-ray photoelectron spectroscopy, the energies of the F_{1s} bond are virtually equal to the arithmetic mean of the energies of the bonds of glass components.¹⁰⁴ Todotoki *et al.*⁶⁸ studied the up-

conversion luminescence[¶] of Er^{3+} in the glass $48\text{InF}_3\cdot 24\text{PbF}_2\cdot 24\text{BaF}_2\cdot 3\text{LaF}_3\cdot 1\text{ErF}_3$ and found that the local frequency of vibrations in the vicinity of Er^{3+} ions ($260\pm 10\text{ cm}^{-1}$) is considerably lower than the mean frequency of the phonon spectrum of the matrix ($470\pm 5\text{ cm}^{-1}$) as determined by Raman scattering. The EPR data on transition metal ions (Cr^{3+} , Ti^{3+} , Fe^{3+} , Mn^{2+} , Co^{2+} , Cu^{2+}) in the glass $25.2\text{PbF}_2\cdot 22.5\text{BaF}_2\cdot 44\text{InF}_3\cdot 3.7\text{SrF}_2\cdot 3.8\text{YF}_3\cdot 0.8\text{AlF}_3$ provide evidence of their octahedral surrounding.¹⁰⁵

Important information on the structures of glasses is provided by spectroscopic methods. In the IR and Raman spectra of fluoroindate glasses, there are bands corresponding to the vibrational modes of isolated octahedra $[\text{InF}_6]^{3-}$.^{106, 107} According to the interpretation of the data from vibrational spectroscopy for the IZBS glass,¹⁰⁶ its structure contains isolated octahedra $[\text{InF}_6]^{3-}$. Later, the octahedral coordination of In^{3+} was con-

¶ The up-conversion is the ionic fluorescence at a shorter wavelength than that of the acting laser radiation.

firmed for the series of glasses $60\text{InF}_3 \cdot 40\text{BaF}_2$, $40\text{InF}_3 \cdot 20\text{ZnF}_2 \cdot 20\text{SrF}_2 \cdot 15\text{BaF}_2 \cdot 5\text{CdF}_2$ and $20\text{InF}_3 \cdot 40\text{ZnF}_2 \cdot 20\text{SrF}_2 \cdot 15\text{BaF}_2 \cdot 5\text{CdF}_2$. A suggestion was put forward about the high content of vertex-bound octahedra in the binary glasses and the transition to almost unbound structures in the multi-component glasses.^{108, 109} The vibrational modes of the octahedra $[\text{ZnF}_6]^{4-}$ and $[\text{InF}_6]^{3-}$ lie close to each other. Ignat'eva *et al.*¹⁰⁷ studied glasses in the system $\text{RF}_3\text{--PbF}_2\text{--MF}_2$ ($\text{R} = \text{Ga}, \text{In}$; $\text{M} = \text{Zn}, \text{Mn}, \text{Ba}$). Analysis by IR and Raman spectroscopy showed that the glasses contain octahedral groups $[\text{InF}_6]^{3-}$ and $[\text{GaF}_6]^{3-}$, the degree of their polymerisation being higher in the fluorogallate glasses. Based on the analysis of the IR spectra in the system $\text{PbF}_2\text{--BaF}_2\text{--AlF}_3\text{--InF}_3\text{--LiF}$, Ignat'eva *et al.*¹¹⁰ suggested that their structures consist of frameworks formed by the octahedra. Upon successive substitution of AlF_3 for InF_3 , starting approximately from the ratio 1 : 1 (~ 15 mol.% of AlF_3), aluminium fluoride forms an independent framework in the glass close to the structural motif in the crystalline $\text{Pb}_3\text{Al}_2\text{F}_{12}$. Incorporation of lithium fluoride disturbs the degree of connectivity of polyhedra in the glass. The fluoroindate glass $15\text{BaF}_2 \cdot 40\text{InF}_3 \cdot 20\text{ZnF}_2 \cdot 20\text{SrF}_2 \cdot 2\text{NaF} \cdot 3\text{GdF}_3$ underwent destruction as the degree of polymerisation of octahedra was increased judging from the IR spectra (devitrification upon polymerisation).⁷⁶

Bureau *et al.*¹¹¹ used precision ^{19}F NMR spectroscopy to investigate glasses in the system $\text{BaF}_2\text{--PbF}_2\text{--InF}_3$ (PBI) and $48\text{PbF}_2 \cdot 25\text{ZnF}_2 \cdot 27\text{InF}_3$ (PZI). They found that three types of fluoride ions contribute to the chemical shift: the ions unbound to the glass former, the ions present in isolated octahedra around the glass-forming atom and the bridging fluoride atoms binding the octahedra to each other. The relative contents of these ions are 5%–11%, 62%–68% and 21%–32% for the PBI glasses and 11%, 37% and 52% for the PZI glasses. The dimensionality of octahedral formations for PZI is 2D, whereas for PBI it is in the interval between 1D and 2D.

Thus, according to the classification based on c.n. of the glass-forming cation,¹¹ the fluoroindate glasses, like the aluminate ones, may be referred to the octahedral glasses. Upon replacement $\text{Al} \rightarrow \text{Ga} \rightarrow \text{In}$, the degree of the glass polymerisation decreased on the whole (it depends strongly on the particular glass composition).

A number of complex fluoroindate glasses include different glass formers. Presumably, these glasses have complex micro-heterogeneous structures. Azkargorta *et al.*¹¹² studied properties of the glass $30\text{BaF}_2 \cdot 18\text{InF}_3 \cdot 12\text{GaF}_3 \cdot 20\text{ZnF}_2 \cdot 9\text{LuF}_3 \cdot 6\text{ThF}_4 \cdot 4\text{MnF}_2 \cdot 1\text{NdF}_3$. Emission of the stimulated radiation at two wavelengths, *viz.*, 1050.2 and 1054.9 nm, was obtained for the laser transition $^4F_{3/2} \rightarrow ^4I_{11/2}$, which suggests the existence of two spatially separated subsystems with different coordination surroundings of the neodymium ions.

V. Properties and prospects for the application of fluoroindate glasses

Refractive indices of fluoroindate glasses ($n \simeq 1.5$) are somewhat higher than those of the ZBLAN glasses (see Table 1); the values of Abbe numbers ($v \simeq 80$), which characterise the dispersion of refractive indices, correspond to the values of this parameter for the fluorozirconate glasses. In the generalised v – n diagram, the fluoroindate glasses occupy approximately the same area as the fluorozirconate glasses.¹¹³ The dispersion of refractive indices of glasses of the types BIZYTh and IZBS was measured.^{72, 114} The refractive indices and dispersions, as well as the theoretical minima of optical losses,¹¹⁵ can be calculated from the molecular increments.¹¹³ Upon addition of Pb^{2+} and Bi^{3+} , the refractive indices of these glasses increased, while upon substitution of Ga^{3+} for In^{3+} they decreased on the contrary⁷² (like upon substitution of Hf^{4+} for Zr^{4+} in the fluorozirconate glasses).

The values of heat and thermal conductivities in fluoroindate glasses are $\sim 20\%$ higher than those in ZBLAN, but are approximately the same magnitude lower than those in majority of

silicate and phosphate glasses.¹¹⁶ Studies of the stress relaxations for the glass $40\text{InF}_3 \cdot 20\text{SrF}_2 \cdot 16\text{BaF}_2 \cdot 20\text{ZnF}_2 \cdot 2\text{GdF}_3 \cdot 2\text{NaF}$ at temperatures below T_g showed that this process is strongly influenced by the atmospheric moisture.¹¹⁷ Characteristics of some fluoroindate glasses are presented in Table 2.

Table 2. Densities (d), heat capacities (C) and thermal conductivities (λ) of some fluoroindate glasses.¹¹⁶

Composition (mol.%)	d /g cm ^{−3}	C /J g ^{−1} K ^{−1}	$10^3 \lambda$ /W K ^{−1} cm ^{−1}
$30\text{PbF}_2 \cdot 15\text{InF}_3 \cdot 15\text{ZnF}_2 \cdot 20\text{GaF}_3 \cdot 20\text{CaF}_2$	5.359	0.67	10.4 ± 0.9
$34\text{InF}_3 \cdot 20\text{ZnF}_2 \cdot 20\text{SrF}_2 \cdot 16\text{BaF}_2 \cdot 6\text{GaF}_3 \cdot 4\text{NaF}$	4.761	0.67	9.9 ± 0.8
$40\text{InF}_3 \cdot 20\text{ZnF}_2 \cdot 20\text{SrF}_2 \cdot 16\text{BaF}_2 \cdot 2\text{GdF}_3 \cdot 2\text{NaF}$	4.753	0.67	10.2 ± 0.8

As it was mentioned above, smooth pyrohydrolysis of indium fluoride complicates the preparation of high-quality glasses, the appearance of oxofluoride phases inducing devitrification. Jha *et al.*⁸³ studied the influence of the fluorinating atmosphere on the quality and stability of the glass $15\text{InF}_3 \cdot 20\text{GaF}_3 \cdot 30\text{PbF}_2 \cdot 20\text{CdF}_2 \cdot 15\text{ZnF}_2$ in the course of its casting. The best samples were obtained when SF_6 was added to nitrogen as the carrier gas, whereas the flow of hydrogen fluoride had a somewhat weaker effect. The poorest effect was produced by ammonium hydrogen fluoride.

In studies of the possibility of the use of fluoroindate glasses as the laser matrices, spectroscopic data on the following dopant ions were analysed: UO_2^{2+} (Ref. 118), Er^{3+} (Refs 84, 119–121), Nd^{3+} (Refs 85, 122–125), Pr^{3+} (Refs 126–128), Tm^{3+} (Refs 129–131), Cr^{3+} (Ref. 132), Yb^{3+} (Ref. 133) and Eu^{3+} (Refs 125, 134). The non-linear effects appearing upon the laser radiation in fluoroindate glasses doped with erbium and neodymium were studied.^{121, 135}

The up-conversion was studied in the glasses activated by Nd^{3+} (Ref. 136), Tm^{3+} (Refs 131, 137), Yb^{3+} (Ref. 138), $\text{Yb}^{3+} + \text{Er}^{3+}$, $\text{Yb}^{3+} + \text{Tm}^{3+}$ or $\text{Yb}^{3+} + \text{Pr}^{3+}$ (Refs 139–141).

In order to increase the pumping efficiency of praseodymium lasers used for the fibre amplifiers at 1.3 μm , it was proposed to coactivate (sensitise) the fluoroindate glasses containing ytterbium with a third rare-earth element, *viz.*, neodymium or erbium.^{16, 17}

When selecting the cladding for the glass $30\text{BaF}_2 \cdot 18\text{InF}_3 \cdot 12\text{GaF}_3 \cdot 20\text{ZnF}_2 \cdot 10\text{YbF}_3 \cdot 6\text{ThF}_4 \cdot 4\text{ZrF}_4$, Rigout *et al.*³⁸ found that the addition of 10 mol.% of KF , 3 mol.% of NaF (instead of a part of BaF_2) and 6 mol.% of AlF_3 (instead of $\text{InF}_3/\text{GaF}_3$) led to $\Delta n = 1.53\%$ with virtually the same coefficients of thermal expansion and T_g . The critical cooling rate is somewhat increased (20 instead of 6 K min^{−1}). Soufiane *et al.*⁷² selected the compositions of the core and claddings of glasses of the IZIBS type by varying n by way of incorporation of GaF_3 and PbF_2 : $\Delta n = 0.24\%$ was achieved.

Jiang *et al.*³² described the selection of the cladding for the fluoroindate fibres. Good results were obtained for fluorophosphate glasses in combination with the GIPCZ glass. The components of the glass fibre, $29\text{PbF}_2 \cdot 3\text{PbCl}_3 \cdot 15\text{InF}_3 \cdot 20\text{GaF}_3 \cdot 13\text{ZnF}_2$ (the core) and $20\text{NaPO}_3 \cdot 10(\text{NH}_4)_2\text{HPO}_4 \cdot 40\text{ZnF}_2 \cdot 15\text{PbF}_2 \cdot 15\text{BaF}_2$ (the cladding), have close values of T_g and the coefficients of thermal expansion. Both glasses mix in unlimited proportions.

The technology of manufacture of the optical fibres based on the fluoroindate glasses is making good progress. The first fibres based on the BIZYbT glass had the optical losses of $\sim 10\,000$ dB km^{−1}.¹⁴² For the fibres based on the BIGaZYbTMn glass this value was already 500 dB km^{−1}.²⁶ Soufiane *et al.*⁷² reported the fabrication of an optical fibre with

losses of 400 dB km⁻¹ at 1.2 µm. Kanamori *et al.*¹⁴³ described the technology of preparation of single-mode fibres with a length up to 500 m from fluoride glasses of the system InF₃–GaF₃–PbF₂–BaF₂–SrF₂–LaF₃–YF₃–LiF–NaF. Based on the fluoroindate glass doped with Pr³⁺ with $\Delta n = 3.6\%$, the minimum level of optical losses was achieved (114 dB km⁻¹ at a wavelength of 1.23 µm). The coefficient of signal amplification at the wavelength 1.3 µm is 0.18 dB mW⁻¹. This is sufficient for these fibres to be used as laser amplifiers, although the level of optical losses is very far from the theoretical level and is fivefold higher than the level achieved for the optical fibre based on ZBLAN. The reason for such a difference seems to be latent crystallisation. In order to decrease the optical losses, it is necessary to enhance the resistance of glasses to crystallisation and to increase the degree of purification from oxygen-containing admixtures.

Itoch *et al.*¹⁴⁴ used a single-mode fibre with the core from the glass 18 InF₃·20 GaF₃·32 PbF₂·10.5 ZnF₂·10.5 CdF₂·4 LaF₃·5 HfF₄ doped with Pr³⁺ and the cladding from the ZBLAN glass. The main characteristics of this fibre are: $N_A \approx 0.55$ at 0.6 µm, the optical losses are 150–250 dB km⁻¹, the coefficient of signal amplification is 0.29 dB mW⁻¹ at 1.3 µm. Optical amplifiers based on fluoroindate glasses doped with Nd³⁺ (Ref. 145) and Pr³⁺ (Ref. 146) have been described.

There are prospects for the use of planar and channel waveguides based on the fluoride glasses, including the fluoroindate glasses, as elements of solid lasers. The idea is to create surface structures with high refractive indices. P de Melo *et al.*¹⁴⁷ obtained such a structure by diffusion of silver ions from the AgF film deposited on the surface of fluoroindate glass. Ionic exchange was observed¹⁴⁸ (Na⁺ for Li⁺ and K⁺) in the glass 15 BaF₂·18 InF₃·12 GaF₃·20 ZnF₂·10 YbF₃·10 ThF₄·15 NaF dipped in the melts of salts. An increase in the refractive index was found in both cases, although judging from the bulk samples,⁷³ the incorporation of potassium instead of sodium should rather decrease the value of n . The effect observed was explained by the mechanical stresses. Josse *et al.*¹⁴⁹ used the surface pyrohydrolysis (treatment with the water vapour): the refractive index increased owing to the ionic substitution of OH⁻ for F⁻. The surface structure was applied by the photolithography method. The fluoride films for planar waveguides can be obtained by physical vapour-phase deposition.⁸⁰

Fluoroindate glasses, particularly those enriched in lead fluoride, are characterised by rather high fluorine ion conductivities,¹⁵⁰ which are however smaller than the conductivities of the crystalline phases of analogous compositions. High mobility of fluorine ions was detected in fluoroindate glasses by the ¹⁹F NMR spectroscopy.^{107, 151, 152} For the glasses of the type IZBS and 40 RF₃·40 BaF₂·20 YbF₃, the ionic conductivity was observed to decrease^{82, 153} upon replacement of indium by gallium and then aluminium. Costa *et al.*¹⁵⁴ studied the mechanical properties of fluoroindate glasses.

VI. Conclusion

In contrast to the fluorozirconate glasses, the compositions of fluoroindate glasses cannot be regarded as optimised. Apparently, in the multicomponent systems involving InF₃ there are several concentration-dependent regions of the stabilities of glasses. It was found that the replacement of InF₃ by GaF₃, BaF₂ or SrF₂ induced a stabilising polycationic effect; however, the possibility of isomorphous substitutions of PbF₂ for BaF₂ has not been studied systematically. It should be noted that the following techniques have a potential in a search for the optimum composition of glasses, *viz.*, the multifactorial design of experiment, the addition of a new component until a new crystalline phase appears as described by Mukhin and Gutkina^{10, 155} and physicochemical analysis including prognostication of the coordinates of multicomponent eutectics.¹⁵⁶

The statements about the higher chemical and thermal stabilities of fluoroindate glasses compared to the fluorozirconate

glasses are questionable. Great discrepancies (by two orders of magnitude) in the determination of the critical cooling rates of multicomponent fluoroindate glasses suggest non-reproducibility of the technology of their preparation. The proneness of InF₃ to hydrolysis determines the instability of these glasses and optical losses in the range of 2.0–3.2 µm.

According to the data from vibrational spectroscopy, fluoroindate glasses are characterised by lower degrees of polymerisation of octahedra than fluorogallate and fluoroaluminat glasses. The reasons for this phenomenon are unclear.

The fields of possible applications of fluoroindate glasses have been little studied. Optical transparency over a wide spectral range, comparatively high density and the possibility of doping with different activators increase the prospects of the practical applications of fluoroindate glasses. It is expedient to investigate the possibility of the production of scintillation materials (including those doped with cerium) with the short decay time.¹⁵⁷ Owing to high concentration of indium fluoride, fluoroindate glasses may be applied for the creation of scintillation media for the neutrino detection.⁹⁶ In order to manufacture highly efficient readjustable lasers, it seems attractive to co-activate fluoroindate glasses with neodymium and chromium ions.

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Solution-free methods for the determination of the molecular mass distribution of polymers

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Abstract. The known methods for the assessment of the molecular mass distribution of bulk polymers are considered. These are based on the analysis of the melt flow curves, the frequency dependence of the relaxation modulus, the shape of the free induction decay curve (pulse nuclear magnetic resonance spectroscopy) and the temperature dependence of compliance in the region of the rubbery elasticity plateau (thermomechanical analysis). The bibliography includes 121 references.

I. Introduction

The molecular mass (MM) and molecular mass distribution (MMD) are important structural characteristics which determine many physical properties of polymers.

Various methods are used for the determination of MM; however, only a few of them can be applied to assess MMD. Gel permeation chromatography (GPC)¹ is the most popular, since it is simple, fast in operation, reliable and relatively cheap. Other methods, in particular, those based on fractionation of a polymer, are time-consuming. All methods are based on analysis of the properties of dilute solutions. Therefore, MMD of many insoluble polymers cannot be assessed at all. This holds for, *e.g.*, polymer networks, where it is desired to know the size distribution of linear chain segments between cross-link points. On the other hand, a method based on destruction of polymers has been developed.² However, this method has found no practical use since it is laborious and requires preliminary establishment of the destruction mechanism, which itself is a rather complicated problem.

Attempts at using the relaxation properties of bulk polymers for the determination of MMD are also known. To this end, studies aimed at finding the relation between MMD and the relaxation time spectrum of a polymer were carried out. In this review, the results of such studies carried out over the last three decades are analysed.

Several short reviews devoted to the studies on the assessment of MMD based on the analysis of the relaxation properties of polymers have been published.^{3–10} However, the authors dwelled, as a rule, on one particular approach without comparing different methods of attacking the problem.

II. The direct problem

To find the MMD function from relaxation data, one should know the dependence of the relaxation properties of polymers on their MMD. This problem has rather long been posed;^{11–17} however, no unambiguous solution has been found so far. Because of this, mixing rules of the contributions of polymer fractions to the relaxation properties are widely used. Theoretical prerequisites to the use of this approach can be found mainly in the reptation theory.^{14, 17, 18} For instance, it is suggested that the time dependence of the relaxation modulus, $G(t)$, be described by the following expression¹⁸

$$G(t) = G_0 \varphi(t) \mu(t),$$

where G_0 is the modulus of elasticity in the region of the rubbery elasticity plateau; $\varphi(t)$ is the function which takes into account the tube renewal, $\mu(t)$ is the probability that motion of an arbitrarily chosen segment of a polymer chain is confined to a deformed tube. For a monodisperse system,

$$\mu(t) = \frac{8}{\pi^2} \sum_{p=1,3,\dots} p^{-2} \exp\left(-\frac{p^2 t}{\lambda}\right) \equiv \mu_1\left(\frac{t}{\lambda}\right),$$

where p is the summation index (an odd number), t is the current time, λ is the maximum relaxation time for the Doi–Edwards model.¹⁷ For a binary polymer blend, a linear mixing rule of the weight fractions w_i of each component is valid

$$\mu(t) = w_1 \mu_1\left(\frac{t}{\lambda_1}\right) + w_2 \mu_2\left(\frac{t}{\lambda_2}\right).$$

An analogous linear mixing rule has been used in other studies.^{19–21}

A more complex $G(t)$ dependence based on the double reptation model has been proposed^{22–25}

$$G(t) = \left[\sum_i w_i G_i^{1/2}(t) \right]^2.$$

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Maier *et al.*²⁶ suggested a generalised empirical formula for calculating the time dependence of the relaxation modulus

$$G(t) = G_0 \left[\int_{\ln M_e}^{\infty} F^{1/\beta}(t, M) w(M) d \ln M \right]^\beta. \quad (1)$$

Here, $F(t, M)$ is the function which describes the relaxation behaviour of a polymer fraction with $MM = M$, t is the current time, β is the parameter characterising the mixing rule and M_e is the MM of a chain segment between entanglements.

The results obtained using different theoretical models were compared with the experimental data on the relaxation behaviour of binary polystyrene blends.²⁶ It was shown that dependence (1) fits the experimental data best with $\beta = 3.84$ virtually irrespective of the form of the function $F(t, M)$. In addition to the above-mentioned theoretical models,^{18, 22–25} the step²⁷ and exponential²⁸ functions and an empirical function containing a finite number (up to 25) of exponential terms with an empirical relaxation time spectrum (the so-called BSW spectrum)²⁹ were also considered. The last-mentioned function was found from the relaxation data for monodisperse specimens. It was found that none of the models considered described adequately the relaxation curves of both polymer blends and even monodisperse polymeric systems. This is consistent with the conclusions reported in a recent study³⁰ in which the results of calculations using the Doi–Edwards model were compared with the experimental results obtained for monodisperse polystyrene specimens.

Empirical mixing rules found mainly in the studies on the analysis of relaxation properties of binary blends of monodisperse polymers are applied to the relaxation time spectrum $H(\lambda)$ (λ is the relaxation time), which is defined as follows:

$$G(t) = \int_{\lambda_{\min}}^{\lambda_{\max}} H(\lambda) \exp\left(-\frac{t}{\lambda}\right) d\lambda.$$

The simplest relation proposed by Ninomiya³¹ has the form

$$H(\lambda) = \sum_{i=1}^N w_i H_i \left(\frac{\lambda}{A_i} \right),$$

where $H_i(\lambda)$ is the relaxation time spectrum of a monodisperse polymer; A_i is the time shift factor due to intermolecular interaction between polymers (such an interaction facilitates the relaxation of the components with higher MM and hampers the relaxation of the components with lower MM). Attempts at taking into account these interactions by deriving generalised formulae lead to sophisticated expressions^{32–34}

$$H(\lambda) = \sum_{i=1}^N \sum_{j=1}^N w_i w_j H_{ij} \left(\frac{\lambda}{A_{ij}} \right),$$

$$H(\lambda) = \sum_{i=1}^N \sum_{j=1}^N \sum_{k=1}^N w_i w_j w_k H_{ijk} \left(\frac{\lambda}{A_{ijk}} \right),$$

which seem to be hardly applicable in practice.

No simpler is yet another relationship^{35, 36}

$$H(\lambda) = \sum_{i=1}^N B_i H_i \left(\frac{\lambda_i}{A_i} \right), \quad (2)$$

where $B_i = w_i^2 + w_i \sum_{j=i+1}^N a_{ij} w_j$ is the form factor,^{37, 38}

which is a function of MM, and $H_i \left(\frac{\lambda_i}{A_i} \right)$ is the BSW spectrum, namely,²⁹

$$H(\lambda_i) = n \left(\frac{\lambda_i}{\lambda_{\max}} \right)^n h \left(1 - \frac{\lambda_i}{\lambda_{\max}} \right),$$

n is a constant ($n < 1$) and h is the Heaviside step function.

Table 1. Characteristics of components and parameters A_i and B_i of Eqn (2) for a binary polystyrene blend.³⁹

M_1	M_2	w_2^a	B_2	A_1	A_2
38900	427000	0.00	0.000	1.00	—
38900	427000	0.01	0.003	1.06	0.030
38900	427000	0.03	0.005	1.17	0.045
38900	427000	0.05	0.007	1.50	0.060
38900	427000	0.10	0.020	1.78	0.070
38900	427000	0.20	0.050	2.89	0.110
38900	427000	0.40	0.170	3.89	0.230
38900	427000	1.00	1.000	—	1.000
23400	2810000	0.01	0.00100	0.90	0.00023
38900	2810000	0.01	0.00080	1.10	0.00100
72400	2810000	0.01	0.00055	1.00	0.00650
124000	2810000	0.01	0.00040	1.20	0.04000

^a $w_1 + w_2 = 1$.

As an example, Table 1 lists the values of the parameters of Eqn (2) taken from Ref. 39. As can be seen, the parameters A_i and B_i depend on the composition and MM of the polymer blend and on the ratio of MM of the blend components. It was also found that all these characteristics affect the values of the maximum relaxation time of each component. This can be exemplified in the data of a study on the relaxation of polymer chains by infrared dichroism⁴⁰ (Table 2).

Table 2. Maximum chain relaxation time (s) in a binary blend of deuterated and hydrogenated polyisoprene.⁴⁰

Content of a high-molecular-mass component (vol. %)	λ_L (for H + L blend)	λ_M (for L + M blend)	λ_H (for M + H blend)
10	20	2.8	50
20	60	3.5	70
30	120	4.5	130
50	150	6.4	160
75	180	6.7	186
100	210	7.0	210

Note. H, M and L denote the blend components with high (370×10^3), medium (125×10^3) and low (53×10^3) molecular mass, respectively.

No general rule exists which would allow passage from the relaxation properties of monodisperse polymers to those of polydisperse polymers. This is largely due to the lack of a theory which can give an adequate description of the dynamic behaviour of polymeric systems.⁴¹ Currently, there is no unique solution of the direct problem of obtaining a relaxation time spectrum based on a particular model or the relaxation properties of a known blend of monodisperse fractions. Obviously, this severely hampers the solution of the inverse problem, consisting of finding the MMD of a polydisperse polymer from its relaxation characteristics.

III. Relations between rheological properties and molecular mass distribution of polymers

Much attention has been paid to the studies on the relations between MMD and viscosity (η) of polymer melts and concentrated solutions.^{12, 42} Most often, this problem was solved by relating the viscosity to the number-average ($\bar{M}_n$), or weight-average ($\bar{M}_w$), or a high-level-average MM ($\bar{M}_z$), or even to their combination (e.g., $\bar{M}_n \bar{M}_z / \bar{M}_w$).

These approaches have not been supported by any theoretical concepts. Attempts to represent the relation between viscosity and MMD in the form

$$\eta \propto \left(\sum_i M_i^\alpha \right)^{1/\alpha},$$

where α characterises the dependence of viscosity on the MM of a monodisperse polymer,

$$\eta \propto M^\alpha$$

are equally unjustified.

An attempt to find a physically substantiated method relating the rheological properties and MMD of a polymeric system has been undertaken.⁴³ This approach was based on the following assumptions: (i) the relaxation time spectrum is limited by the maximum relaxation time $\lambda_{\max}(\dot{\gamma})$, where $\dot{\gamma}$ is the shear rate; (ii) the maximum relaxation time is inversely proportional to the shear rate; (iii) the maximum relaxation time of a given polymer is affected by the presence in the blend of another polymer with a lower MM and (iv) the relaxation time spectrum of a given polymer is independent of the type of polydispersity of the polymer.[†]

Based on these assumptions, the following formula relating the MMD function to the viscosities of the polymer fractions was derived⁴³

$$\sum_{i=m+1} w_i = \left[\left(\frac{\eta_{m+1}}{K} \right)^{1/3.4} - \left(\frac{\eta_m}{K} \right)^{1/3.4} \right] (M_{m+1} - M_m)^{-1}, \quad (3)$$

where w_i is the weight fraction of a polymer fraction with MM = M_i , η_m is the viscosity of a polymer with MM = M_m , K is the coefficient in the equation relating the viscosity of a monodisperse polymer to its MM

$$\eta = KM^{3.4}.$$

Hence it follows that

$$w_m = \left(\frac{1}{K} \right)^{1/3.4} \left(\frac{\eta_m^{1/3.4} - \eta_{m-1}^{1/3.4}}{M_m - M_{m-1}} - \frac{\eta_{m+1}^{1/3.4} - \eta_m^{1/3.4}}{M_{m+1} - M_m} \right). \quad (3a)$$

Expression (3a) was used for analysing a number of binary blends and commercial polystyrene specimens.⁴⁴ It was shown that the polydispersity indices,

$$\gamma = \frac{\bar{M}_w}{\bar{M}_n},$$

determined by rheological methods are close to those found by GPC.

A physical substantiation of the rheological approach has been given by Malkin and Teishev^{45–47} who used the phenomenon of flow separation in monodisperse polymers, discovered by Vinogradov,⁴⁸ as the basis for their consideration. Mathematically, this phenomenon can be described by the relation

$$\eta(\dot{\gamma}) = \begin{cases} \eta_0 & \text{for } \tau \leq \tau_s \\ \tau_s / \dot{\gamma} & \text{for } \tau > \tau_s. \end{cases}$$

Here η_0 is the highest Newtonian viscosity and τ_s is the stress at which flow separation occurs in the polymer.

Based on the known relationship,

$$\eta_0 = KM^a,$$

Malkin and Teishev derived the formula^{45, 46}

$$\eta(\dot{\gamma}) = \left[\int_0^{M(\dot{\gamma})} (KM^a)^{1/a} f(M) dM + \left(\frac{\tau_s}{\dot{\gamma}} \right)^{1/a} \int_{M(\dot{\gamma})}^0 f(M) dM \right]^a, \quad (4)$$

where the integration limit is

$$M(\dot{\gamma}) = \left(\frac{\tau_s}{K\dot{\gamma}} \right)^{1/4},$$

and $f(M)$ is the MM function.

Formula (4) can be used for unimodal MMD functions which include a small number of parameters (Malkin and Teishev⁴⁶ analysed the Bisley, lognormal and other two-parameter distribution functions). In this case, the melt flow curve is sufficiently sensitive to the parameters of the distribution function.

Gordon and Shaw⁴ calculated the MMD function using another analytical expression for the flow curve, namely,

$$\eta(\dot{\gamma}) = \begin{cases} \eta_0 & \text{at } \tau \leq \tau_s \\ \dot{\gamma}^{-v} & \text{at } \tau > \tau_s, \end{cases}$$

where τ_s (and, correspondingly, $\dot{\gamma}_s$) defines the point of transition from Newtonian to a non-Newtonian flow and v is the exponent in the power law of the melt flow

$$\eta \propto \dot{\gamma}^{-v}.$$

The position of this point depends on the MM of the polymer.

The procedure for the calculation of the MMD function depends on which mixing rule for viscosities is used. Gordon and Shaw considered the following mixing rule:

$$\log \eta = w_1 \log \eta_1 + w_2 \log \eta_2.$$

Using this mixing rule, the relation between the integral MMD function $F(M)$ and parameters of the melt flow curve has the form

$$F(M) = 1 + \frac{1}{v} \frac{d \ln \eta}{d \ln \dot{\gamma}} \Big|_{\dot{\gamma}=g(M)},$$

where the function $g(M)$ relates the shear rate to the MM of the polymer and the parameter v .

A more general mixing rule,

$$\eta^{1/a} = w_1 \eta_1^{1/a} + w_2 \eta_2^{1/a}$$

leads to the following formula,

$$F(M) = 1 + \frac{1}{v} \left(\frac{\eta}{\eta_0} \right)^{1/a} \left(\frac{\dot{\gamma}}{\dot{\gamma}_s} \right)^{v/a} \frac{d \ln \eta}{d \ln \dot{\gamma}} \Big|_{\dot{\gamma}=\dot{\gamma}_s M^{-a/v}},$$

where

$$m = \frac{M}{\bar{M}_w}.$$

An algorithm and software for calculations of the MMD function using the last two formulae have been published in a monograph.⁴ It should be noted that the exponent a is not known with certainty. Recently,⁴⁹ it was shown that the parameter a depends on the shear rate (and frequency) in such a manner that its magnitude decreases from values in the range between 3 and 5, which is typical of low shear rates (the highest Newtonian viscosity), down to 0 for high shear rates (the lowest Newtonian viscosity). Moreover, it was empirically found that the parameter a depends also on MMD of the polymer as follows

$$a = \beta_0 + \beta_1 \left(\frac{M_h}{M_l} \right), \quad (5)$$

where $\beta_0 = 3.39 \pm 0.37$, $\beta_1 = 0.03 \pm 0.04$, and M_h and M_l are the MM of the high-molecular and low-molecular mass components of a binary polymer blend, respectively. The values of the

[†]This assumption seems to be not universally true for systems with entanglements.

coefficients of equation (5) also vary to a certain degree depending on the type of the polymer.

With some grounds, it is believed^{44, 46} that the rheological approach can hardly be used for characterisation of an arbitrary MMD function; however, the authors of a monograph (Ref. 4) have a more optimistic view on these things.

IV. Methods based on dynamic measurements

Attempts at using the frequency dependences of the real and imaginary parts of the relaxation modulus of elasticity for the determination of the MMD of polymers have long been undertaken. Ninomiya and Fujita seem to be the first who reported studies in this line of investigation as long ago as 1957.^{50–52} This approach is based on theoretical or empirical relationships between the relaxation time spectrum and MM of polymers^{12, 13, 53} (see also Section II).

In the simplest form, the theory of polymer dynamics was reported by Rouse who developed the well-known single-chain model which is basic to the studies by Ninomiya.^{31, 50–52, 54, 55} More recent investigations⁵⁶ were based on the Doi–Edwards model in which interchain interaction is considered as interweaving of polymer chains, or entanglements, which confine mainly lateral displacements of the polymer chains.

The results of studies carried out on monodisperse specimens of different polymers and their blends (for the most part, binary blends)^{26, 39, 40, 57–61} can be outlined as follows.

For polymers with narrow MMD, the log-log plots of the frequency dependence of the real part of the relaxation elasticity modulus, $G'(\omega)$, nearly coincide in the high-frequency region (the region of the rubbery elasticity plateau). Marked distinctions are observed in the region of low-frequency ‘tails’ where $G'(\omega)$ depends on ω as

$$G'(\omega) \propto \omega^2.$$

The ‘tails’ can be matched by using a shift factor proportional to MM raised to a certain power; it is commonly accepted^{12, 13, 62, 63} that the exponent value lies between 3.4 and 3.7.

The frequency dependences of the imaginary part of the relaxation modulus of elasticity, $G''(\omega)$, pass through a maximum. The position of the maximum depends on MM of a polymer in the same way as the low-frequency ‘tails’ of the $G'(\omega)$ and $G''(\omega)$ curves.

In binary polymer blends, the polymer fractions possess similar relaxation properties; however, no complete coincidence with the behaviour of monodisperse systems is achieved. That is, the low-frequency ‘tails’ are shifted towards higher frequencies for the component with the higher MM and towards lower frequencies for the component with the lower MM.

This phenomenon is associated with the interchain interaction (coupling effect, nematic interaction),^{39, 40, 64–68} which also manifests itself as the orientation of low-molecular-mass chains (even oligomers) in the bulk of the oriented high-molecular-mass matrix.

It should be noted that this frequency shift should occur even in the absence of intermolecular interaction. Indeed, let the relaxation properties be determined by the only relaxation time, which is of course dependent on the MM of the high-molecular-mass fraction. Then, for $\omega \rightarrow 0$, the real part of the relaxation modulus of elasticity of a binary polymer blend takes the form

$$G'(\omega) = w_1 \frac{\omega^2 \lambda_1^2}{1 + \omega^2 \lambda_1^2} + w_2 \frac{\omega^2 \lambda_2^2}{1 + \omega^2 \lambda_2^2} \rightarrow \omega^2 (w_1 \lambda_1^2 + w_2 \lambda_2^2).$$

Obviously, it is this effect that should be observed if $\lambda_1 > \lambda_2$, namely, a shift of the relaxation moduli of elasticity of the high-molecular-mass and low-molecular-mass fractions towards high and low frequencies, respectively. An analogous relationship is also valid for $G''(\omega)$, for $\omega \rightarrow 0$

$$G''(\omega) = w_1 \frac{\omega \lambda_1}{1 + \omega^2 \lambda_1^2} + w_2 \frac{\omega \lambda_2}{1 + \omega^2 \lambda_2^2} \rightarrow \omega (w_1 \lambda_1 + w_2 \lambda_2).$$

The aforesaid can be illustrated by the corresponding plots shown in Fig. 1. On the other hand, a direct mutual effect of the polymer fractions (see Table 2) cannot also be ruled out.

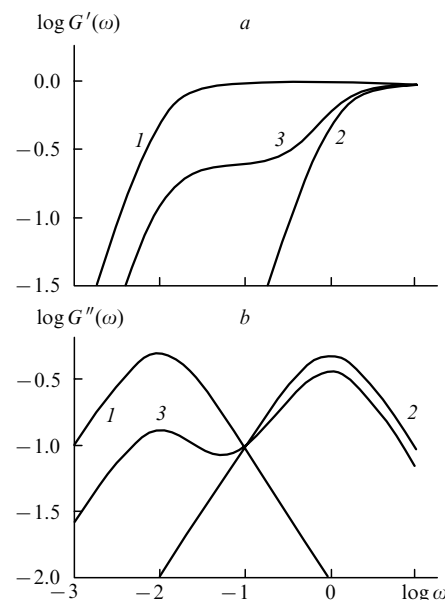


Figure 1. Frequency dependences of the real (a) and imaginary (b) parts of the relaxation modulus of elasticity for specimens with one relaxation time of 100 (1) and 1 arbitrary unit (2) and for their blend containing 25% of the first component (3).

A salient feature of the $G'(\omega)$ and $G''(\omega)$ curves of binary blends is that the height of the rubbery elasticity plateau (in the first case) and that of the peak (in the second case) depend on the relative concentration of components. Similarly to the $G(t)$ curve, a ‘step’ appears on the $G'(\omega)$ curves. The $G''(\omega)$ curves are characterised by two peaks and the peak height ratio depends on the ratio of the blend components.

However, data on the relation between the peak heights and the concentration of the blend components are contradictory. Different authors use different formulae. For instance, a linear dependence was suggested⁶⁹

$$G(t) = w_1 G_1 \left(\frac{t}{d_1} \right) + w_2 G_2 \left(\frac{t}{d_2} \right);$$

the parameter d is associated with the coupling effect.

Other (mainly quadratic) types of mixing rules have also been suggested.^{13, 70–72} For instance, based on the concept that each polymer fraction can be characterised by a frequency corresponding to the MM of the fraction and that at lower frequencies the contribution of this fraction to the relaxation modulus can be neglected, a procedure was developed²⁶ for the determination of the MMD function taking into account a quadratic dependence of the real part of the relaxation modulus of elasticity on the concentration of the high-molecular-mass component. Each fraction makes a contribution

$$w_i = \left[\frac{G'(\omega_i)}{G_0} \right]^{1/2}.$$

Comparison of the results obtained using this procedure with those obtained by GPC showed²⁷ that for binary polymer blends the dynamic approach is less accurate than the rheological method based on the analysis of the melt flow curve.

The complex viscosity, $\eta^*(\omega)$, was also proposed^{44,49} to be used for assessing the MMD function.

$$\eta^*(\omega) = \frac{\sqrt{[G'(\omega)]^2 + [G''(\omega)]^2}}{\omega}.$$

In the high-frequency region (for $\omega \rightarrow \infty$), the complex viscosity decreases nearly proportionally to ω^{-2} , whereas in the low-frequency region (for $\omega \rightarrow 0$) it takes the limiting value corresponding to the highest Newtonian viscosity. It is in the low-frequency region that the strongest dependence of $\eta^*(\omega)$ on MMD of a polymer melt is observed and the parameter a [see Eqns (4) and (5)] has the maximum value. Thus, the frequency dependence of viscosity is similar to the dependence of viscosity on the shear rate, which corresponds to the Cox–Merz rule.¹²

Comparison of different approaches to the solution of the problem of determining the MMD function allowed Tuminello and Cudre-Mauroux⁴⁴ to conclude that the best results can be obtained by analysing the frequency dependence of the complex viscosity; it was also found that analysis of the real part of the relaxation modulus of elasticity gives overestimated, whereas analysis of the imaginary part gives underestimated values.

Investigations on the relaxation of dielectric properties are widely used for studying the relaxation properties of polymers. The relation between dielectric properties and MMD has been analysed^{73–77} taking *cis*-polyisoprene as an example. It was shown that in this case the dielectric loss function can be predicted with ease if the autocorrelation function of a single chain, the mixing rule and the MMD function are known. Difficulties arise when considering the inverse problem. An attempt has been undertaken⁷⁷ to find the MMD function from the dielectric relaxation data using the Tikhonov regularisation, which was previously used for calculating the relaxation time spectra.^{78,79} This study was carried out assuming a linear mixing rule and that the MMD function is described by the Flory–Schulz equation

$$f(M) \propto M^v \exp\left(-\frac{M}{M_n}\right).$$

Information on the width of MMD can be obtained from the analysis of the effective relaxation time⁸⁰ in the low-frequency region or, in other words, of the low-frequency ‘tails’ of the $G'(\omega)$ and $G''(\omega)$ curves. Indeed, assuming that the relaxation time of a monodisperse polymer depends on its MM,

$$\lambda = KM^a,$$

for $\omega \rightarrow 0$ we get

$$G'(\omega) \approx G_0 \omega^2 \sum_i w_i \lambda_i^2 = G_0 \omega^2 K^2 \sum_i w_i M_i^{2a},$$

$$G''(\omega) \approx G_0 \omega K \sum_i w_i M_i^a.$$

Hence

$$\langle \lambda \rangle_2 \equiv \frac{G'(\omega)}{G''(\omega)} = \omega K \frac{\sum_i w_i M_i^{2a}}{\sum_i w_i M_i^a} = \omega K \langle M^a \rangle_2,$$

$$\langle \lambda \rangle_1 \equiv \frac{G''(\omega)}{G_0} = \omega K \sum_i w_i M_i^a = \omega K \langle M^a \rangle_1.$$

The subscripts 2 and 1 on the mean values of λ and MM correspond to a greater degree of averaging in the former case and to a lesser one in the latter. The ratio of the mean values can serve as a measure of the width of MMD. This algorithm is analogous to that which is commonly accepted for assessing the width of MMD and uses the mass-average and number-average MM and their ratio as the polydispersity index; the difference is that in the latter case $a = 1$ (in the relaxation method, $a \approx 3-4$).

Of course, it should be kept in mind that even monodisperse polymers possess a relaxation time spectrum; as a rule, the higher the MM the broader the relaxation time spectrum.²⁹

V. Spin-spin relaxation technique (pulse NMR spectroscopy)

Both rheological and relaxation approaches have been used for the analysis of the MMD of linear polymers. For polymer networks, a steady flow is impossible. However, analysis of stress relaxation data (especially, of the frequency dependences of the relaxation modulus) can be used for extracting information on the MMD of chains of a polymer network. This was done using the spin-spin relaxation technique (pulse NMR spectroscopy).^{81–89}

At sufficiently high temperatures ($T > T_g + 100$), the dependence of the free induction decay on time is given by the following expression

$$G(t) = \int_1^N \int_0^{\pi/2} \{ [g(N, \theta, t) P(N) \sin \theta] d\theta \} dN, \quad (6)$$

where N is the number of segments (the chain length) and θ is the angle between the vector connecting the chain ends and the direction of external magnetic field.

$$g(N, \theta, t) \approx \exp \left[-\omega_1^2 (3 \cos^2 \theta - 1)^2 t^2 \frac{\ln N}{N^2} \right],$$

where ω_1 is the second moment of the free induction decay curve, expressed in frequency units.

In the time domain, the free induction decay has a long slowly descending component. The initial portion of this component contains information on MMD, while the length of its ‘tail’ is proportional to the average length of the chain segment between entanglements and inversely proportional to the current time t . Hence it follows that one can assess the MMD for those chains which are shorter than the length of the chain segment between entanglements (N_0). As was shown experimentally,⁸⁵ $N_0 \approx 10^5$ segments. It should be noted that no independent determination of the chain segment length was performed, which introduces an error into the results obtained. However, even assuming that the segment is a unit of the polymer chain, this method can be applied to those linear polymers for which MM is much higher than 10^6 .

An essential result obtained in a series of studies^{85–89} is that formula (6) can be used for assessing MMD of chain segments between entanglements in polymer networks. At $T > T_g + 100$, intermolecular interaction has almost no effect on the relaxation of sufficiently long chains with the number of segments $N > 10$. Hence the curve of the free induction decay characterises the MMD of chain segments between entanglements. In this case, the integral of the function $G(t)$ can be represented in a linearised form

$$F(t) = \int_0^t G(t_1) dt_1 \approx -0.03 \langle N^2 \rangle + \langle N \rangle t \frac{\pi}{2\sqrt{3}}.$$

The coefficients of this equation define the polydispersity index of the chains of the polymer network, γ_n :

$$\gamma_n = \frac{\overline{M}_{nw}}{\overline{M}_{nn}} = \frac{\langle N^2 \rangle}{\langle N \rangle^2}$$

(the index n indicates that the chains of the polymer network are considered).

Thus, the analysis of the curve of the free induction decay makes it possible to assess MMD of both linear polymers and chain segments between entanglements of the polymer network.

The theoretical conclusions have been confirmed experimentally taking poly(tetrahydrofuran) with isocyanate end groups as an example.⁹⁰ In this case, the polymer network resulted from a trimerisation reaction,⁹¹ which would ensure identical MMD for both the initial prepolymer and chain segments between entanglements. Comparison of the GPC data on MMD of poly(tetrahydrofuran) macromolecules with the results of NMR studies on MMD of the chains of the polymer network made it possible to

draw a conclusion that NMR spectroscopy can be effectively used in this case.

Pulse NMR spectroscopy was used for studying the MMD of the chains in different polymer networks depending on the conditions of the synthesis,⁸⁸ as well as the evolution of MMD during ageing⁹² and at thermal^{92,93} and mechanical⁹⁴ destruction.

Limitation on the use of NMR spectroscopy for assessing the MMD of the chains of polymer networks with low concentration of nodes is due to the fact that entanglements behave as chemical cross-link points, which leads to the anisotropy of the molecular motion of chain segments. This limitation is similar to that which appeared in the determination of the equilibrium modulus of elasticity of polymer networks: for networks with low node concentration, the number of nodes is equal to the sum of chemical (covalent) cross-link points and topological entanglements.^{95–102}

In highly cross-linked polymer networks, the effective dipole-dipole interaction is determined not only by the interaction of protons in the same chain, as is theorised; an appreciable contribution comes also from the interaction between protons of different chains. This imposes some limitations on the use of NMR spectroscopy. Finally, one should keep in mind that the model network considered here has a simple topology (chains linked by tri- or tetrafunctional cross-link points), whereas the real network contains 'tales', small rings, a sol fraction and other defects responsible for considerable uncertainty of the relaxation time spectra of a polymer.^{95, 103, 104}

VI. Thermomechanical analysis

Usually, thermomechanical curves of polymers are analysed based on the concepts of the relaxation time spectrum and the temperature dependence of relaxation times.¹² It is this approach that has been used for the rationalisation of (i) the relation between the temperature dependence of the extent of the rubbery elasticity plateau and the MM of linear polymers discovered by Kargin and Slonimskii¹⁰⁵ and (ii) such an important relation as the Williams–Landel–Ferry formula.¹³ It is the relaxation nature of deformation phenomena that is responsible for the fact that the shape of a thermomechanical curve is 'sensitive' to the polydispersity of a polymer.¹⁰⁶

Recently,¹⁰⁷ a procedure for solving the direct problem, which implies theoretical determination of the flow point (temperature) of a linear polymer, T_f , under conditions of thermomechanical analysis (TMA) from the structure and MM of the polymer, has been proposed. However, the authors were rather sceptical of the possibility of using TMA for the determination of MMD of polymers.

On the other hand, such a possibility has been demonstrated.^{108, 109} Physical substantiation^{110–113} of the approach used was based on the model of a network of physical links.^{41, 114}

In its most explicit form, the relaxation modulus (compliance or deformation at a given stress) can be related to the MMD of a polymer using the classical theory of rubbery elasticity of polymer networks and the temperature dependence of the concentration of physical nodes.¹¹⁰ However, an analysis¹¹² showed that the concentration of nodes formed by weak intermolecular bonds cannot vary substantially in a rather narrow temperature range between the glass transition temperature and the flow point (for linear polymers) or the temperature at which the equilibrium modulus is attained for covalent polymer networks (the extent of the rubbery elasticity plateau). Much stronger is the temperature dependence of the lifetime of the nodes as well as the dependence of the relaxation of the polymer chain conformations on the temperature–time superposition. Irrespective of the details of the physical pattern of the phenomenon, the kinetic law can be to sufficient accuracy expressed by a step function.¹¹⁰ Relaxation

occurs in a narrow time range near the characteristic relaxation time, which depends on the MM of a polymer or a chain segment between entanglements of the polymer network.

If mechanical properties of a system are considered according to the Kelvin–Voigt model, the following formulae relating the function $\varphi(T)$ containing information on MMD to compliance (deformation) are valid:

for a linear polymer

$$\varphi(T) = \frac{J_T - J_0}{J_T}, \quad (7)$$

for a polymer network

$$\varphi(T) = \frac{J_T - J_0}{J_T} \frac{J_{eq}}{J_{eq} - J_0},$$

where J_T , J_{eq} and J_0 is the compliance at a given temperature, the equilibrium compliance (for a polymer network) and the compliance of a hypothetical polymer with infinite MM, respectively.

The function $\varphi(T)$ is in essence the integral MMD function expressed in terms of the flow point of a chain with a given MM rather than the MM of a polymer fraction:

$$\varphi(T) = \sum_{i=1}^{\infty} w_i \delta_i(t, T),$$

$$\delta_i(t, T) = \delta[t - \lambda_i(T)] = \begin{cases} 0 & \text{for } t < \lambda_i(T) \\ 1 & \text{for } t \geq \lambda_i(T), \end{cases}$$

$\lambda_i(T)$ is relaxation time of the chain conformation. The J_0 value characterises that part of the temperature dependence of the modulus of elasticity (compliance) which is unaffected by the MM and MMD of the polymer and serves as a basis for the calculations of the function $\varphi(T)$ [see Eqn (7)].

Schematically, the procedure for the determination of $\varphi(T)$ using the temperature dependence of deformation (compliance) of a linear polymer is shown in Fig. 2. From the rod displacement with respect to the dilatometric curve *1* one can determine the J_0 value (in rod displacement units, this is the value h_0 calculated as the difference between the corresponding points on curves 2 and *1*) and compliance J , which is proportional to h calculated as the difference between the corresponding points on curves 3 and *1*.

The main problem of TMA studies is to determine the relation between the temperature and MM, *i.e.*, to pass from the function $\varphi(T)$ to the integral MMD function $\varphi(M)$. Such a relation can be found after choosing a particular mixing rule. As in many cases considered above, it seems reasonable to assume that the relaxation time of a chain conformation with a given MM is independent

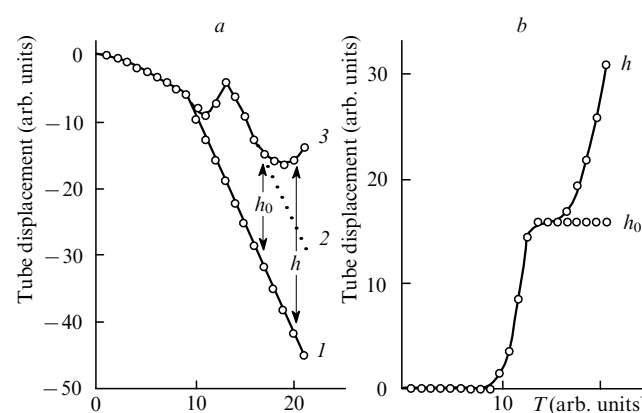


Figure 2. Rod displacement (h) curves obtained in TMA studies. Experimental curves (*a*) and difference between the rod displacement and dilatometric curves (*b*). Dilatometric curve (*1*), hypothetical curve for a polymer with infinite MM (*2*) and the real rod displacement curve (*3*).

of whether it is a monodisperse or a polydisperse polymer. As can be seen, this problem is common to all methods for the determination of the MMD function.

At first glance, if this condition is met, the problem seems to be simple. That is, one needs to find a relation between the extent of the rubbery elasticity plateau,

$$\Delta T = T_f - T_g$$

and MM. However, constructing this dependence faces some difficulties. The first problem is to determine the basic function, $J_0(T)$. This requires studying the temperature dependence of the deformation of model polymer specimens with narrow MMD and high MM in the region of the rubbery elasticity plateau. Here, it is encouraging that such a dependence is rather weak,^{110, 113} so to a sufficient accuracy the function $J_0(T)$ can be considered constant.

Yet another problem is associated with the fact that the temperature range corresponding to passage from the rubbery elasticity plateau to the flow of a polymer is rather wide and depends on both the MM and MMD of the polymer. That is why several formulae for calculating the function $\Delta T(M)$ were derived, e.g., the Kargin–Slonimskii formula¹⁰⁵ and a number of similar formulae,¹⁰⁹ e.g.:

for polar polymers

$$\log M = 1.6 + \frac{20\Delta T}{200 + \Delta T},$$

for non-polar polymers,

$$\log M = 2.0 + \frac{10\Delta T}{100 + \Delta T}.$$

In a recent study¹¹³ of monodisperse specimens of poly(oxyethylene glycol) with low-molecular masses (1500–12000), a rather sharp transition from the rubbery elasticity plateau to the flow of a polymer was observed and a calibration curve was constructed in the form

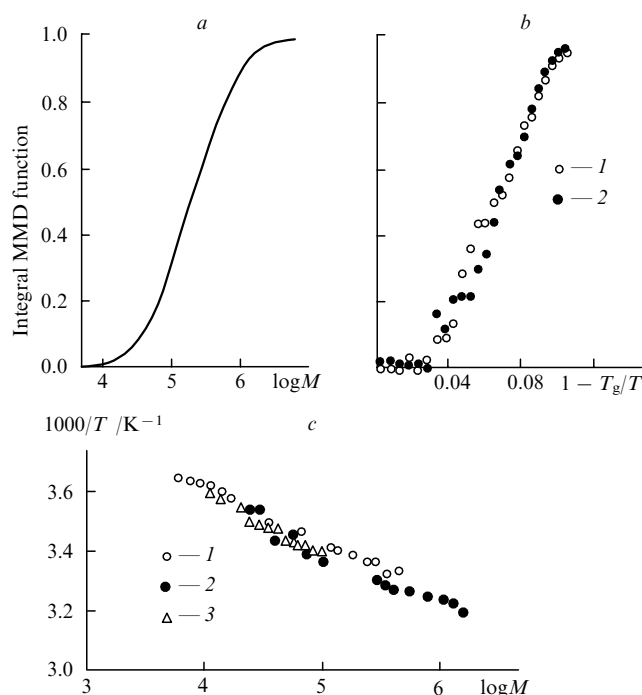


Figure 3. Integral MMD functions (a, b) and calibration curve (c) for amorphous polypropylene.¹¹⁵ Obtained from GPC (a) and TMA (b) studies. Rod load, g: 0.5 (1), 2.0 (2). 10^{-3} MM: 180 (a, b); c: 52 (1), 189 (2) and 330 (3).

$$\ln M = A + B \left(1 - \frac{T_g}{T} \right). \quad (8)$$

It was found that for a wide array of polymers $A \approx 3$ and $B \approx 17$.

A calibration procedure was proposed,¹¹⁵ which refers to a polymer with an arbitrary MMD characterised by, e.g., GPC. To this end, the integral curve $\varphi(M)$ is compared with the integral curve $\varphi(T)$ which can be constructed in the $\varphi(T) - T_g/T$ coordinates. By comparing the MM and T values corresponding to the same value of the integral fraction it is possible to find the relation between MM and temperature, i.e., to construct a calibration curve for a wide range of MM using the data for one polymeric specimen.

The integral MMD curve of amorphous polypropylene is shown in Fig. 3a and the dependence $\varphi(T)$ in the coordinates of Eqn (8) is shown in Fig. 3b. The calibration curve (Fig. 3c) was constructed by comparing the MM and T values. As can be seen, the results obtained for three samples of polymers with different MM give a versatile dependence of the type (8).

Thermomechanical analysis can be applied to different types of loading of polymeric specimens, among which penetration and tension are the most popular.^{106, 113}

VII. Conclusion

Consideration of 'solution-free' approaches to the determination of MMD of polymers proposed by different authors shows that, in essence, there are no well-developed methods so far. First of all, this is due to the fact that the inverse problem, viz., determination of the relaxation time spectrum and, hence, the MMD of a polymer from the relaxation data, belongs to the so-called ill-posed mathematical problems.^{26, 47, 77–79, 116–118} Attempts at solving the problem require some *a priori* statements or experimental establishment of the relaxation time spectrum (or other property, e.g., viscosity or the flow point) with the MM of a polymer. In essence, it is this point to which all the approaches discussed above come. Regularisation methods for solving ill-posed problems,¹¹⁹ as applied to the problem of determining the relaxation time spectrum or, more particularly, the MMD of a polymer^{77–79, 117, 118} are also based on certain assumptions (see, e.g., Ref. 77).

Baumgarten *et al.*²⁹ derived the relaxation time spectrum (the so-called BSW spectrum) of monodisperse polystyrene specimens without any preliminary postulates by analysing the relaxation data using IRIS software (see Ref. 120). More recently, the BSW spectrum was used for the description of the relaxation properties of polybutadiene.^{38, 39} Empirical constants characterising the BSW spectrum, as well as the relaxation time spectrum itself, have no theoretical substantiation and it is unclear to what extent the expansion of the function $G(t)$ in exponents is unique.

It is likely, the lack of a well-founded theory which takes into account mutual effects of polymers with different MM is the most serious obstacle to the development of a relevant relaxation method for the determination of MMD of polymers. Similarly to the Rouse and Doi–Edwards theories, such a theory would help to obtain an exact relation between the MM and the corresponding relaxation time. An empirical relation,

$$\lambda(M) \propto M^\alpha,$$

where $\alpha \approx 3.4$ casts some doubt since there are strong reasons (see, e.g., Refs 30, 41, 80, 121) to believe that $\alpha = 4$.

Thermomechanical analysis seems to be the most promising method. Probably, mutual effects of polymers are more pronounced in isothermal (rheological and frequency) experiments than in the studies on the temperature dependence of deformation parameters. The relaxation time spectrum uniquely characterises both the frequency and temperature dependences of the relaxation properties of a polymer. However, as was shown experimentally, the relation between the flow point and the MM of a polymer is

much more pronounced than the relation between the frequency (time) of this transition and MM.

Further development of 'solution-free' methods will open prospects for the determination of MMD of polymer blends and composite matrices. This may give an impetus to scientific research in this area.

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Structural and dynamic properties of tetrahydroborate complexes

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Abstract. Data on the structures of tetrahydroborate complexes from X-ray diffraction analysis, neutron and electron diffraction, and IR and NMR spectroscopy are considered. It is shown that, in addition to the diversity of stabilising ligands, complexes of Group III and IV transition metals are characterised by diverse types of coordination of terminal (η^1 , η^2 and η^3) or bridging (between neutral molecular units) tetrahydroborate groups. Compounds with BH₄ groups with different denticities can be found among these complexes. Most tetrahydroborates of these metals in the oxidation states +3, +4 comply with the principle of maximum occupancy of the coordination sphere. Tetrahydroborates of Group III and IV metals exhibit clear-cut stereochemical non-rigidity (fluxionality): the protons of the BH₄ ligand are equivalent on the NMR time scale. Group I and V–VIII transition metals mainly form η^2 -complexes, which are stereochemically much more rigid than complexes of Group III and IV metals. It is suggested that electronic configuration of the central atom is the crucial factor determining different structures and stereochemical behaviours of the tetrahydroborate complexes. Data on the structures and properties of post-transition and s-element tetrahydroborates are also consistent with this assumption. The bibliography includes 248 references.

I. Introduction

Coordination compounds containing the simplest hydroborate anion BH₄[−] as a ligand possess many practically valuable properties. Tetrahydroborate complexes are used as selective reducing agents, starting compounds in the syntheses of complex and organometallic derivatives, precursors for the production of borides, hydrides and other inorganic materials, and as catalysts of hydrogenation, isomerisation, oligomerisation, polymerisation, *etc.* In addition, these complexes exhibit unusual structural and dynamic properties such as the ability to form metal–hydrogen–boron multicentre bonds and exceptionally low barriers to

the intramolecular exchange of bridging and terminal hydrogen atoms in the tetrahydroborate ligand.

In mononuclear complexes, a tetrahydroborate ligand either exists as the BH₄[−] ion or is linked to the metal through one, two or three M–H–B bridges (η^1 , η^2 and η^3 coordination, respectively). The forms of coordination of tetrahydroborate ligands in polynuclear complexes are even more diverse. The BH₄[−] anion is isoelectronic with a methane molecule. Therefore, it has been suggested that tetrahydroborates can serve as structural models for some steps in the activation of C–H bonds in saturated hydrocarbons. The existence of complexes with η^1 -, η^2 - and η^3 -BH₄ ligands has been proven by various structural methods. However, the NMR spectra of many tetrahydroborate complexes point to the equivalence of the four protons in the BH₄ group, which indicates that these compounds are fluxional, *i.e.* bridging and terminal protons of the tetrahydroborate ligands are able to undergo fast (on the NMR time scale) intramolecular exchange.^{1–5} Thus, most of tetrahydroborate complexes constantly exist in the state of fast dynamic transformation, resulting in the change of the mutual orientation of the complex-forming ion and the tetrahydroborate ligand.

Numerous attempts have been made to explain the unusual properties of tetrahydroborate complexes by such factors as the influence of the Coulomb interaction between the metal ion and the anion, the tendency of the central atom to fill its outer electron shell, the influence of stabilising ligands and so on. A great deal of information on the structures of tetrahydroborates of light elements was provided by *ab initio* quantum-chemical calculations. For transition metal complexes, these calculations are quite cumbersome and have now been performed for only a few objects. It is often impossible to determine unambiguously the most favourable configuration of the complex on the basis of calculations because the energies of different types of coordination of BH₄ ligands differ only slightly; therefore, the results of calculations need to be compared with experimental data (see several papers^{6–10} and references therein).

Tetrahydroborate complexes of various metals have been studied to different extents. The structures of tetrahydroborates of Group III and IV transition metals, especially uranium derivatives, and titanium and zirconium compounds have been studied in most detail. Complexes formed by Group I and V–VIII transition metals and by alkali, alkaline earth and post-transition metals are less studied. Therefore, this review starts with a brief characterisation of the physical properties of tetrahydroborate

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complexes and methods for their investigation; the ability of various ligands to stabilise transition metal tetrahydroborates is also considered. This is followed by discussion of the structural and dynamic properties of tetrahydroborates of Group III and IV transition metals with terminal BH_4 ligands and comparison of these properties with the properties of Group I and V–VIII transition metal complexes. An attempt is made to interpret the regularities observed. Data on the structure of alkali, alkaline earth and post-transition metal tetrahydroborates and polynuclear complexes with bridging BH_4 groups are used to verify and refine the correlations found. The results of determination of the structures of tetrahydroborate complexes by electron, X-ray and neutron diffraction analyses and by IR spectroscopy as well as the data on the complexes of Group IV–VIII transition metals, for which the type of coordination of tetrahydroborate ligands has been characterised by NMR spectroscopy, are summarised in tables. Less reliable data on the ligand denticity based only on the results of IR spectroscopy and not confirmed by diffraction methods are cited as little as possible, only where it is necessary to complete the picture.

Hundreds of studies dealing with the investigation or application of tetrahydroborate complexes are published annually. About 200 of these complexes have been structurally characterised; new experimental results have been obtained for them in recent years. However, the questions of what factors determine the structural (type of coordination) and dynamic (stereochemical rigidity or fluxionality) properties of the BH_4 ligands in the complexes and whether or not these properties are related to one another (if they are related, what is the type of relationship) still remain to be answered.

In this review, we analyse the results of experimental determination of the type of coordination of BH_4 groups in different types of complexes by electron, neutron and X-ray diffraction analyses and by NMR spectroscopy. The results are used to make an assumption about the main factors determining the structural and dynamic features of tetrahydroborate complexes.

II. General characteristics of tetrahydroborate complexes

Compounds containing tetrahydroborate ligands are known for all Group IA, IIA and IIIA metals and for all transition metals, except for technetium, promethium, platinum, gold, francium, radium and some actinides, mainly of the berkelium subgroup.^{1–5} The results of studies of metal tetrahydroborate complexes by various methods are summarised in Tables 1–3. The formal oxidation numbers of metal atoms in these complexes vary from 0 to +4. Some metals can form the complexes in two different oxidation states [for example, Cu(I) and Cu(II), Yb(II) and Yb(III), U(III) and U(IV), *etc.*]; for titanium, complexes containing the central atoms in four different oxidation states (0, +2, +3, +4) have been structurally characterised. The ion radii of metal cations (r_i) in tetrahydroborates can differ by a factor of more than six [for example, for Be(II), $r_i = 0.27 \text{ \AA}$, and for Cs(I), $r_i = 1.67 \text{ \AA}$],²²² the surface area of the coordination sphere can differ by a factor of ~ 40 and the volume of the central atom, by a factor of 200. The BH_4^- ($r_i = 2.04 \text{ \AA}$) anion markedly exceeds in size any metal cation which forms complexes with it.¹ Depending on the nature of the central atom, the stabilising ligands and conditions, the compounds in question can be solid, liquid, or gaseous. In the crystalline state, tetrahydroborates having ionic, molecular, islet (ion-molecular) and polymeric (oligomeric) structures are known. Diamagnetic and paramagnetic tetrahydroborate complexes, both low- and high-spin ones, for example $(\text{TMEDA})\text{Cr}(\eta^2\text{-BH}_4)_2$ with $\mu_{\text{eff}} = 4.8 \mu_{\text{B}}$,⁹³ are known. Some tetrahydroborates are stable in air but most of them are unstable and decompose, often with an explosion, in the presence of air or moisture.

An important characteristic of tetrahydroborate complexes is the manner in which the BH_4 ligand is attached to the central atom. The structures of these complexes are determined most often using X-ray diffraction analysis. In many instances, this method can be used to determine the position of hydrogen atoms and establish the type of ligand coordination. The range of structurally characterised compounds includes complexes with

Table 1. Structurally characterised complexes with terminal BH_4 ligands.

Complex	Distance /Å			Vibration frequencies of the BH ₄ group (IR spectroscopy) /cm ^{−1}	Ref.
	M–H _b	M···B	B–H _b		
Complexes of Group III and IV transition metals					
Sc(η ² -BH ₄)(η ³ -BH ₄) ₂ (THF) ₂	2.09(5) m	2.330(5) (η ³) 2.229(5) (η ³) 2.551(5) (η ²)	1.08(5) m	2508, 2420, 2377, 2304, 2242, 2154, 2061, 1348, 1250, 1185, 1124, 1044	11, 12
[(Me ₃ Si) ₂ C ₅ H ₃] ₂ Sc(η ² -BH ₄)	2.03(4)	2.52(2)	1.19(4)	2415, 2125	13
Y(η ² -BH ₄)(η ³ -BH ₄) ₂ (THF) ₃		2.58 (η ³) 2.68 (η ²)	—	—	14
Y(η ³ -BH ₄) ₃ · 2 THF				2482, 2300, 2220, 2165, 1250, 1192, 1103, 1042	12, 15
[Y(η ³ -BH ₄) ₄] [−]	—	2.41 m	—		
[Y(η ³ -BH ₄) ₂ (THF) ₄] ⁺	—	2.52 m	—		
(MeOCH ₂ CH ₂ C ₅ H ₄) ₂ Y(η ² -BH ₄)	2.26(5), 2.27(5)	2.773	1.11(5), 1.11(5)	2419, 2367, 2294, 2226, 2197, 2174	16
(EtMe ₄ C ₅) ₂ Y(η ² -BH ₄)(THF)	2.35 m	2.669(4)	—	—	17
La(BH ₄) ₃ · 3.5 THF				—	18
[La(η ³ -BH ₄) ₂ (THF) ₅] ⁺	2.47, 2.59, 2.28	2.730(2)	0.94, 1.15, 1.12	—	
[La(η ² -BH ₄) ₂ (η ³ -BH ₄) ₂ (THF) ₂] [−]	2.43, 2.74, 2.55, 2.40, 2.55	2.760(2) (η ³) 2.900(2) (η ²)	0.93, 0.96, 1.49 1.03, 1.13		
(MeOCH ₂ CH ₂ C ₅ H ₄) ₂ Pr(η ³ -BH ₄)	—	2.757(18)	—	2404, 2254, 2190	19
(MeOCH ₂ CH ₂ C ₅ H ₄) ₂ Nd(η ³ -BH ₄)	—	2.664(25)	—	2404, 2260, 2184	19
(Pr ⁱ Me ₄ C ₅) ₂ Sm(η ³ -BH ₄)(THF)	2.36(3), 2.51(3), 2.49(3)	2.624(3)	1.18(3), 1.13(3), 1.13(3)	—	20
(MeOCH ₂ CH ₂ C ₅ H ₄) ₂ Yb(η ² -BH ₄)	—	2.800	—	—	19
[Me ₂ Si(3-Me ₃ SiC ₅ H ₃) ₂] ⁺ Yb(η ³ -BH ₄)(THF)	2.25, 2.22, 2.06	2.470	1.15, 1.20, 1.09	2475, 2385–2240, 2195, 2125	21
Yb(η ³ -BH ₄) ₂ (MeCN) ₄	2.46, 2.52, 2.33	2.666(6)	1.19, 1.05, 1.09	2363, 2310, 1604, 1176, 1109	22

Table 1 (continued).

Complex	Distance /Å			Vibration frequencies of the BH ₄ group (IR spectroscopy) /cm ^{−1}	Ref.
	M – H _b	M···B	B – H _b		
Complexes of Group III and IV transition metals					
Yb(η ³ -BH ₄) ₂ (Py) ₄	—	2.692(4)	—	2390, 2360, 2342, 2337, 2248, 2216, 1948, 1876, 1869	22
U(η ² -BH ₄)(η ³ -BH ₄) ₂ (DMPE) ₂	—	2.84(3) (η ²) 2.68(4) (η ³)	—	2440, 2360, 2340, 2300, 2200, 1125	23
U(η ³ -BH ₄) ₃ (Ph ₂ Ppy) ₂	—	2.61(2) 2.656(8)	—	2420, 2300, 2200, 1120	24
(C ₆ Me ₆)U(η ³ -BH ₄) ₃	—	2.54(3) 2.49(4) 2.69(3)	—	2493, 2199, 2122	25
[U(η ³ -BH ₄) ₃ (DME)(μ-H)] ₂	—	2.64(4) 2.53(6)	—	2480, 2210, 2140, 1195, 1170, 1095, 1035	26
[Na(THF) ₆][Cp*U(η ³ -BH ₄) ₃] ₂	—	2.61(2) 2.57(2) 2.68(2) 2.58(2) 2.64(2) 2.59(2)	—	—	27
[U(η ³ -BH ₄) ₂ (THF) ₅][(C ₇ H ₇)U ₂ (η ³ -BH ₄) ₆] [U(η ³ -BH ₄) ₂ (THF) ₅] ⁺	—	2.72(4) 2.71(4)	—	—	28
[U(η ³ -BH ₄) ₃ (C ₇ H ₇)U(η ³ -BH ₄) ₃] [−]	—	2.58(2)	—	—	29
[[UCl ₅ (η ² -BH ₄)]U(η ³ -BH ₄) ₂ (DC18C6)] ₂ [UCl ₅ (η ² -BH ₄)] ^{2−} [U(η ³ -BH ₄) ₂ (DC18C6)] ⁺	—	2.70(9) 2.44(12) 2.69(16)	—	—	29
U(η ³ -BH ₄) ₄ (THF) ₂	2.16, 2.39, 2.70	2.53(6)	1.15, 1.15, 1.15	—	30
U(η ³ -BH ₄) ₂ (η ² -BH ₄) ₂ (Ph ₃ PO) ₂ (C ₆ H ₆)	—	2.55(3) (η ³) 2.75(3) (η ²)	—	—	31
U(η ³ -BH ₄) ₃ (η ² -BH ₄)(Ph ₃ PO) ₂	2.0, 2.5, 2.8 2.0, 2.5, 2.8 2.0, 2.5, 2.8 2.1	2.51(5) (η ³) 2.58(6) (η ³) 2.65(6) (η ³) 2.84(5) (η ²)	—	—	32
CpU(η ³ -BH ₄) ₃	—	2.57(5) 2.46(4)	—	2528, 2156, 2087, 1208	33, 34
Cp ₂ U(η ³ -BH ₄) ₂	—	2.61, 2.58	—	—	35
[1,3-(Me ₃ Si) ₂ C ₅ H ₃] ₂ U(η ³ -BH ₄) ₂	2.42, 2.36, 2.37	2.56(1)	1.13, 1.11, 1.20	2498, 2198, 2120, 1165	36
Cp ₂ *U(η ³ -BH ₄) ₂	—	2.58(3)	—	—	37
Cp ₃ U(η ³ -BH ₄)	—	2.48	—	—	38
(2,4-Me ₂ C ₅ H ₃)U(η ³ -BH ₄) ₃	—	2.50(3) 2.52(3) 2.54(3)	—	2518, 2156, 2090	34
(C ₄ Me ₄ P) ₂ U(η ³ -BH ₄) ₂	2.29(20)	2.553(1)	1.10(15)	—	39
Ind ₂ U(η ³ -BH ₄) ₂	—	2.51(2) 2.53(2)	—	—	40
U(η ³ -BH ₄) ₃ (OCHPh ₂)(THF) ₂	—	2.629(7) 2.587(6) 2.599(9)	—	—	41
U(η ³ -BH ₄) ₂ (OCHPh ₂) ₂ (THF) ₂	2.527(8), 2.483(9), 2.63(1)	2.711(6)	1.115(8), 1.02(3), 1.03(1)	—	41
(tritox)U(η ³ -BH ₄) ₃ (THF)	—	2.51(2) 2.65(2)	—	—	42
(tritox) ₃ U(η ³ -BH ₄)	—	2.58(2)	—	—	42
(COT)U(η ³ -BH ₄) ₂ (OPPh ₃)	—	2.57(1) 2.66(1)	—	—	43
U{PhC[N(SiMe ₃) ₂] ₂ }(η ³ -BH ₄) ₂	2.26(3), 2.27(3), 2.31(3)	—	1.08(2), 1.11(3), 1.12(3)	2509, 2209, 2139	44
[(Me ₃ SiNCH ₂ CH ₂) ₃ N]U(η ³ -BH ₄)(THF)	—	2.68(2)	—	2452, 2256, 2201, 2163, 2135, 1246	45
[(Me ₃ Si) ₂ N] ₃ Th(η ³ -BH ₄)	—	2.61(3)	—	2500, 2345, 2240, 2180	46
Np(η ³ -BH ₄) ₄	2.3(5), 2.1(3), 2.1(3)	2.46(3)	1.0(3), 1.1(2), 1.1(2)	see ^a	47, 48
Ti(η ³ -BH ₄) ₃ (see ^b)	1.984(5)	2.175(4)	1.276(5)	2585, 2400, 2230, 2155, 2030, 1345, 1265, 1210, 1075, 595, 450	49

Table 1 (continued).

Complex	Distance /Å			Vibration frequencies of the BH ₄ group (IR spectroscopy) /cm ⁻¹	Ref.
	M – H _b	M ⋯ B	B – H _b		
Complexes of Group III and IV transition metals					
Ti(η ² -BH ₄) ₃ (DME)	1.93(2), 2.01(2) 1.92(2), 1.87(2) 1.94(2), 1.88(2)	2.424(3) 2.403(2) 2.405(2)	1.22(2), 1.16(2) 1.18(2), 1.16(2) 1.03(2), 1.16(2)	2470, 2420, 2130, 2060	50, 51
Ti(BH ₄) ₃ (PMe ₃) ₂	1.90(6) 1.73(7), 2.25(7), 2.62(7)	2.40(1) 2.27(1)	1.03(7) 0.95(6)	2532, 2401, 2358, 2110	52
Ti(η ² -BH ₄) ₂ (DMPE) ₂	2.04(2), 2.09(2)	2.534(3)	1.15(2)	2332, 2297, 2220, 2138, 2062	53, 54
Cp*Ti(η ² -BH ₄){(Me ₂ PCH ₂) ₃ SiBu ^t }	2.00(5)	2.445(7)	0.98(6), 1.05(5)	—	55
Cp ₂ Ti(η ² -BH ₄)	1.75(8)	2.37(1)	1.23(8)	2438, 2400, 2050, 1940, 1315, 1115	56, 57
Cp ₂ Ti(η ² -BH ₄) (see ^b)	1.89(5)	2.31(4)	—	—	58
[CpTi(η ³ -BH ₄)(μ-Cl)] ₂	1.89, 1.90, 2.05	2.17(1)	1.07, 1.18, 1.11	—	59
{PhC[N(SiMe ₃)] ₂ } ₂ Ti(η ² -BH ₄)	1.92	2.426(4)	1.14	2420, 2395, 2110	60
[(Me ₃ Si) ₂ N] ₂ Ti(η ² -BH ₄)(THF)	2.08(5), 2.13(5)	2.454(4)	—	2440, 2400, 2270, 2195	61
[(Me ₃ Si) ₂ N]Ti(η ² -BH ₄) ₂ (Py) ₂	1.98(4), 2.03(4) 2.059(4), 1.99(4)	2.476(6) 2.482(5)	—	2380, 2340, 2220, 2140	61
{[2,6-Pr ⁱ ₂ C ₆ H ₃ O]Ti(η ³ -BH ₄) ₂] ₂	—	2.166(4) 2.162(4)	—	2569, 2560, 2214, 2139, 2097, 2068	62
[2,6-Pr ⁱ ₂ C ₆ H ₃ O]Ti(η ² -BH ₄) ₂ (PMe ₃) ₂	—	2.457(6) 2.444(6)	—	2412, 2401, 2377, 2368, 2164, 2130	62
[2,6-Pr ⁱ ₂ C ₆ H ₃ O] ₃ Ti(η ³ -BH ₄)	—	2.207(13)	—	2528, 2207, 2196, 2140	62
(Bu ^t NCH = CHNBu ^t)TiCl(η ³ -BH ₄)	1.87(3), 1.90(4), 1.97(3)	2.175(4)	1.12(4), 1.09(4), 1.18(4)	2546, 2173, 2121, 1213	63
(Bu ^t NCH = CHNBu ^t)Ti(η ² -BH ₄)(η ³ -BH ₄)	1.88(3), 1.87(3) 1.90(3), 1.89(3), 1.91(3)	2.304(3) (η ²) 2.175(3) (η ³)	1.08(3), 1.06(3) 1.02(4), 1.07(3), 1.14(4)	2545, 2178, 2099, 1212	63
(BP)Ti(η ³ -BH ₄) ₂	1.978, 1.870, 1.951 1.875, 2.013, 1.984	2.184(7) 2.205(8)	—	2559, 2542, 2209, 2118	64
[Ti(CO) ₄ (η ³ -BH ₄)]-[K(18C6)] ⁺	2.02(4) m	2.158(7)	1.11(2) m	2495, 2132, 2058	65
Zr(η ³ -BH ₄) ₄ (see ^b)	2.211(19)	2.308(3)	1.272(16)	—	66
Zr(η ³ -BH ₄) ₄	—	2.34(3)	—	2567, 2180, 2115, 1286, 1213, 1170, 1098, 1056, 575, 504	67, 68
Cp ₂ Zr(η ² -BH ₄) ₂	—	2.59(2)	—	2431, 2375, 2216, 2137, 1294, 1108	69, 70
[(MeC ₅ H ₄) ₂ Zr(η ² -BH ₄)(THF)][BPh ₄] (see ^c)	1.87(9), 1.93(9) 1.98(9), 1.92(8)	2.54(1) 2.55(1)	1.10(9), 1.30(9) 1.24(8), 1.27(9)	2472–2429, 2119	71
(BP)Zr(η ² -BH ₄)(η ³ -BH ₄)(THF)	2.068, 2.036, 2.162	2.354(8) (η ³)	—	2539, 2458, 2400, 2219, 2117, 2020	64
Zr(η ³ -BH ₄) ₂ {Me ₃ SiN[CH ₂ CH ₂ N(SiMe ₃)] ₂ }	2.125, 1.999 2.04(7), 2.10(5), 2.03(6) 2.21(4), 2.20(8), 2.31(5)	2.572(12) (η ²) 2.370(7)	—	2519, 2494, 2236, 2214, 2162	72
Zr(COT)''(η ² -BH ₄)(η ³ -BH ₄)	—	2.605 (η ²) 2.368 (η ³)	—	—	73
Zr ₂ (COT)'' ₂ (μ-H)(η ³ -BH ₄)	—	2.33(2)	—	—	73
Zr(η ³ -BH ₄)[(3,5-Me ₂ Ph)N(Ad)] ₃	2.16(4), 2.21(4), 2.23(4)	2.400(4)	—	2500, 2234, 2180, 2154	74
Zr ₂ H ₄ (η ² -BH ₄) ₂ (PMe ₃) ₄	2.16(5), 2.20(5)	2.59(1)	—	—	75
Zr ₃ H ₆ (η ² -BH ₄) ₂ (η ³ -BH ₄) ₄ (PMe ₃) ₄	2.05(3), 2.11(4), 2.21(3) 2.14(3), 2.15(4) 2.19(3), 2.12(4) 2.08(3), 2.24(3), 2.08(3) 2.06(4), 2.10(4), 2.19(4) 2.35(4), 2.19(3), 2.11(4)	2.352(4) (η ³) 2.610(4) (η ²) 2.655(4) (η ²) 2.363(6) (η ³) 2.361(6) (η ³) 2.394(6) (η ³)	1.17(4), 1.18(4), 1.19(3) 1.14(4), 1.14(4) 1.14(4), 1.13(4) 1.21(4), 1.10(4), 1.14(4) 1.08(4), 1.03(4), 1.19(4) 1.14(4), 1.12(4), 1.14(4)	2530, 2495, 2430, 2400, 2385, 2320, 2230, 2135, 2095	76
Zr ₂ H ₃ (η ² -BH ₄)(η ³ -BH ₄) ₄ (PMe ₃) ₂	1.98(6), 2.23(7), 2.02(6) 2.05(5), 2.22(6) 2.05(7), 2.17(6), 2.14(5)	2.336(7) (η ³) 2.604(8) (η ²) 2.361(8) (η ³)	1.27(6), 1.05(7), 1.05(6) 1.18(5), 1.03(7) 1.03(8), 1.23(6), 1.01(6)	2550, 2505, 2435, 2390, 2220, 2155, 2102, 1520	77

Table 1 (continued).

Complex	Distance /Å			Vibration frequencies of the BH ₄ group (IR spectroscopy) /cm ^{−1}	Ref.
	M–H _b	M⋯B	B–H _b		
Complexes of Group III and IV transition metals					
Zr ₂ H ₃ (η ² -BH ₄)(η ³ -BH ₄) ₄ (PMe ₃) ₂	2.17(5), 2.04(5), 2.21(5) 2.14(5), 2.09(6), 2.36(7)	2.332(7) (η ³) 2.357(8) (η ³)	1.11(5), 1.19(5), 1.00(5) 1.07(6), 0.97(6), 1.11(7)	2550, 2505, 2435, 2390, 2220, 2155, 2102, 1520	77
Zr ₂ H ₄ (η ² -BH ₄)(η ³ -BH ₄) ₃ (DMPE) ₂	2.32(8), 2.33(9) 2.08–2.47	2.70(1) (η ²) 2.40(2) (η ³)	1.21(10), 1.06(9) 0.94–1.38	2490, 2370, 2300, 2200, 2175, 2140	76
(Bu ^t NCH = CHNBu ^t)Zr(η ³ -BH ₄) ₂	2.26(5), 2.03(4), 2.15(5) 2.09(5), 2.06(4), 2.30(5)	2.380(6) 2.331(5)	1.16(5), 1.04(4), 1.04(6) 1.26(5), 1.11(4), 1.08(5)	2530, 2216, 2109, 1219, 1208	63
Zr ₃ S ₃ (SBu ¹) ₂ (η ² -BH ₄)(η ³ -BH ₄) ₃ (THF) ₂	—	2.53(2) (η ²) 2.33(2) (η ³) 2.35(2) (η ³) 2.35(2) (η ³)	—	—	78
Zr ₆ S ₆ (SBu ¹) ₄ (η ² -BH ₄) ₂ (η ³ -BH ₄) ₆ (THF) ₂	—	2.511(11) (η ²) 2.279(2) (η ³) 2.325(11) (η ³) 2.276(12) (η ³)	—	—	78
Hf(η ³ -BH ₄) ₄ (see ^d)	2.130(9)	2.281(8)	1.235(10)	2570, 2197, 2123, 1290, 1218, 1140, 480	79–81
(MeC ₅ H ₄) ₂ Hf(η ² -BH ₄) ₂ (see ^d)	2.069(7), 2.120(8)	2.553(6)	1.255(9), 1.208(13)	2444, 2398, 2235, 2160, 1340, 1120	82
Hf ₂ H ₃ (η ² -BH ₄)(η ³ -BH ₄) ₄ (PMe ₃) ₂	—	2.33(2) (η ³) 2.53(3) (η ²) 2.34(3) (η ³) 2.35(3) (η ³) 2.32(3) (η ³)	—	2545, 2505, 2430, 2385, 2210, 2160, 2105	77
Hf ₂ (NPP) ₂ H ₃ (η ³ , η ² , η ¹ -BH ₄) ₃	1.93, 2.43 2.01, 2.25 2.25 m	2.636(7) (η ¹) 2.583(6) (η ²) 2.322(8) (η ³)	1.29 m	2520, 2425, 2400, 2144	83
Complexes of Group I and V–VIII transition metals with a bidentate coordination of the BH ₄ ligands					
V(η ² -BH ₄) ₃ (PMe ₃) ₂	1.83(3)	2.365(5)	1.14(3)	2431, 2385, 2353, 2227, 2218, 2087	84, 85
[V(η ² -BH ₄) ₂ (PMe ₃) ₂] ₂ O	1.97(3) m	2.383(6) m	1.15(4) Å.Å.	2408, 2397, 2359, 2229, 2106	85
CpV(η ² -BH ₄)(DMPE)	1.78(4)	2.254(9)	1.17(4), 1.12(8)	2380, 2345, 2255, 1855	86, 87
[V(μ-Cl)(μ-DPPM)(η ² -BH ₄)] ₂	1.78(8), 1.69(10)	2.314(14)	1.24(9), 1.36(10)	—	88
[(Me ₃ Si) ₂ N] ₂ V(η ² -BH ₄)(THF)	1.711(7), 1.916(6)	2.38(2)	0.943, 1.43(7)	2434, 2396, 2240, 2134	89
Cp ₂ Nb(η ² -BH ₄)	2.0	2.26	1.1	2460, 2423, 1745, 1628, 1382, 1162	90, 57
Me ₂ C(C ₅ H ₄) ₂ Nb(η ² -BH ₄)	1.94(7)	2.36(1)	1.25(7)	2461, 2419	91
Ta ₂ (μ-BH ₃)(μ-DMPM)(η ² -BH ₄) ₂ (C ₇ H ₈)	2.16(7), 2.17(7)	2.578(8)	1.09(7), 1.09(7)	—	92
Ta ₂ (μ-BH ₃)(μ-DMPM)(η ² -BH ₄) ₂	1.82(7), 2.25(8) 2.04(8), 2.12(7)	2.539(10) 2.585(10)	1.13(13), 1.19(7) 1.12(8), 1.16(7)	2376, 2341, 2203, 2122, 2090, 2052	92
(TMEDA)Cr(η ² -BH ₄) ₂	1.931, 2.094 1.875, 2.081	2.44(1) 2.42(1)	—	2380, 2230, 2120	93
CrH(η ² -BH ₄)(DMPE) ₂	—	2.45	—	2460, 2430, 2060, 1650, 1060, 2330, 2071, 1056	94 54
Cr(CO) ₄ (η ² -BH ₄)(Ph ₃ P) ₂ N	1.96(7), 1.80(6)	2.29(1)	1.25(8), 1.01(6)	2415, 2365, 2210	95
Mo(CO) ₄ (η ² -BH ₄)(Ph ₃ P) ₂ N	1.99(9), 2.04(8)	2.413(20)	1.26(11), 1.14(9)	2390, 2375, 2330, 2280	96
MoH(η ² -BH ₄)(PMe ₃) ₄	1.96	2.468(12)	1.12	2340, 2290, 1935, 1885, 1360, 1165	97
W(η ² -BH ₄)(CO)(NO)(PMe ₃) ₂	1.8(1), 2.1(1)	2.36(2)	—	2450, 2415	98
Mn(η ² -BH ₄) ₂ (THF) ₃	2.04(4)	2.438(3)	1.1 m	2390, 2140, 1115	99
(Ph ₄ P)[Mn(η ² -BH ₄) ₃ (THF)]	1.95, 1.98 1.95, 2.18 1.87, 2.24	2.368(3) 2.335(2) 2.362(2)	1.10 m	2395, 2210, 2135, 1110	100, 101
FeH(η ² -BH ₄)[MeC(CH ₂ PPh ₂) ₃]	1.58(11), 1.65(11)	2.16(2)	1.32(12), 1.18(10)	2380, 2320, 1910, 1440, 1182	102, 103
RuH(η ² -BH ₄)(PMe ₃) ₃	1.81(4), 1.85(4)	—	—	2383, 2369, 2318, 1932	104
OsH ₃ (η ² -BH ₄)[P(cyclo-C ₅ H ₉) ₃] ₂	1.90	2.30(1)	1.31	2448, 2427, 2130, 2112	105
Co(η ² -BH ₄)(terpy)	1.81(5), 1.80(5)	—	1.44(6), 1.27(4)	2420, 2403, 2325, 2000, 1985, 1927, 1893, 1190	106
Co(η ² -BH ₄)(terpy) (see ^d)	1.707(12), 1.740(12)	—	1.290(9), 1.287(10)	—	106
CoH(η ² -BH ₄)[P(cyclo-C ₆ H ₁₁) ₃] ₂	1.80(8), 1.87(9)	2.14(1)	1.30(7), 1.39(9)	2390, 2368, 1958, 1379	107, 108
Co(η ² -BH ₄)[MeC(CH ₂ PPh ₂) ₃]	1.55(15), 1.45(15)	2.21(3)	1.27(16), 1.38(17)	2370, 2330, 2015	109

Table 1 (continued).

Complex	Distance / Å			Vibration frequencies of the BH ₄ group (IR spectroscopy) / cm ^{−1}	Ref.
	M – H _b	M ⋯ B	B – H _b		
Complexes of Group I and V – VIII transition metals with a bidentate coordination of the BH ₄ ligands					
Rh ₂ (η ² -BH ₄) ₂ (μ-CO)(Ph ₂ Ppy) ₂	—	2.29(5) 2.23(5)	—	2421, 2383, 1383, 1138	110
NiH(η ² -BH ₄)[P(cyclo-C ₆ H ₁₁) ₃] ₂	1.73(5), 1.76(6)	2.201(8)	1.27(5), 1.30(5)	2360, 2050, 2020, 1868, 1140	111, 112
Cu(η ² -BH ₄)(dmphen)	1.58(5)	2.08(2)	—	—	113
Cu(η ² -BH ₄)(dmdphen)	1.50(5)	2.116(12)	—	2385, 2350, 2245, 1982, 1128	114
Cu(η ² -BH ₄)(phen)(PPh ₃) (see ^d)	2.03(9), 1.63(7)	2.29(2)	1.24(3), 1.17(3)	2360, 2330, 2245, 2070, 1910, 1120	114
Cu(η ² -BH ₄)(phen)[P(OEt) ₃]	2.16(10), 1.98(10)	2.34(1)	0.81(16), 0.83(13)	2360, 2330, 2080	115
Cu(η ² -BH ₄)(PPh ₃) ₂	1.82(3)	2.185(6)	1.07(3)	2392, 2350, 2262, 1984, 1924	3, 116
Cu(η ² -BH ₄)(PBuPh ₂) ₂	1.60(10), 1.80(10)	2.20(1)	1.00(10), 1.40(10)	2404, 2394, 1995, 1937, 1139	117, 118
Cu(η ² -BH ₄)(DPPF)	1.65(6), 1.60(6)	2.158(8)	1.17(7), 1.23(6)	2397, 2354, 2013, 1970	119
{CH ₂ N(CH ₂ CH ₂ PPh ₂) ₂ Cu(η ² -BH ₄) ₂ }	1.683, 1.681	2.247(6)	—	2365, 2010, 1120	120
Complexes of Group I and V – VIII transition metals with a monodentate coordination of the BH ₄ ligand					
V(η ¹ -BH ₄) ₂ (DMPE) ₂	1.88	2.833	1.12(3)	2341, 2312, 2110, 2095, 1060	54, 84
Py ₄ Cr(η ¹ -BH ₄) ₂	1.94 2.33	3.253 3.309	1.16 0.98	2300, 2180, 2120, 2080, 1080 – 1040	93
FeH(η ¹ -BH ₄)(DMPE) ₂	1.72	2.84	1.14	2350, 2075, 1060	121 – 123
RuH(η ¹ -BH ₄){Me ₈ [16]aneS ₄ }	1.83	2.895(16)	1.09	2320, 2265, 1055	124
Cu(η ¹ -BH ₄)(PMePh ₂) ₃	1.83(8)	2.578(10)	1.19	2315, 2045, 1060	125, 126
Cu(η ¹ -BH ₄)(PMePh ₂) ₃ (see ^d)	1.697(1)	2.518(3)	1.170(5)	—	125
Cu(η ¹ -BH ₄){MeC(CH ₂ PPh ₂) ₃ }	1.60(4)	2.44(2)	—	2300, 1980	109, 127
Ag(η ¹ -BH ₄)(PMePh ₂) ₃	1.76(7)	2.80(1)	1.2(1)	2300, 2050, 1070	128, 129
Cu(η ¹ -BH ₄) ₂ (Cyclam)	2.28(1)	3.09(1)	0.98(9)	2315, 2227, 2156, 1104	130 – 132
Cu(η ¹ -BH ₄) ₂ (TMAC)	2.25(1)	3.18(1)	1.16(6)	2377, 2333, 2321, 2160, 1118	130 – 132
Complexes of post-transition metals					
Zn(η ² -BH ₄)(Cl)(TMEDA)	1.983(2), 1.963(2)	2.29(2)	—	2422, 2368, 2207, 2120	133
(Ph ₄ P)[Zn(η ² -BH ₄) ₃]	1.80	2.22	1.1	2455, 2438, 2410, 2060	134, 135
V ₂ Zn ₂ (η ² -BH ₄) ₂ (PMePh ₂) ₄	1.78(5), 1.82(5)	—	—	—	136
CpNb(CO)(μ-H)Zn(η ² -BH ₄) ₂	1.839, 1.871 1.736, 1.942	—	0.986, 1.056 1.067, 1.026	2445, 2420, 2100	137
Cd(η ² -BH ₄)[HB(3,5-Me ₂ pz) ₃]	—	2.423(5)	—	2426, 2384, 2037	138
H ₂ Ga(η ² -BH ₄) (see ^c)	1.826	2.179	1.334	—	139
HGa(η ² -BH ₄) ₂ (see ^c)	1.762 – 1.891	2.172	1.250 – 1.456	2566, 2550, 2488, 2478, 2471, 2042, 2026, 1984, 1976, 1971, 1961	140
Me ₂ Ga(η ² -BH ₄) (see ^c)	1.791	2.163	1.217	2540, 2470, 1980, 1922	141, 142
Cp(CO) ₂ FeGa(η ² -BH ₄)(CH ₂) ₃ NMe ₂	—	2.374(3)	—	2419, 2376	143
Me ₂ In(η ² -BH ₄) (see ^c)	—	—	—	—	144
Complexes of s-elements and aluminium					
Li(η ³ -BH ₄)[HC(3,5-Me ₂ pz) ₃]	—	2.223(7)	—	2374, 2314, 2223, 2163	145
[Li(η ¹ -BH ₄) ₂](18C6)	1.7(2)	2.36(3)	1.1(2)	—	146
Li(η ² -BH ₄)(DME) ₂	1.7(2)	2.470(4)	1.17(2)	2373, 2281, 2258, 2134	147
{Li(η ² -BH ₄)(TG)} _∞	—	2.478(6)	—	2560, 2382, 2330, 2295, 2264, 2198	147
Li(η ³ -BH ₄)(THF) ₃	2.02(4), 2.10(5), 2.12(4)	2.319(7)	1.15(3)	2382, 2334, 2272, 2237, 2176, 2127, 2111	147
Li(η ² -BH ₄)(Py) ₃	2.06, 1.90	2.401(7)	1.15, 1.07	2354, 2309, 2279, 2245	148
Li(η ³ -BH ₄)(py*) ₃	2.07, 2.08, 2.26	2.279(4)	1.15, 1.11, 1.12	2231, 2230, 2209, 2149	148
Li(η ² -BH ₄)(coll) ₂	1.83	2.252(6)	1.17(2)	2421, 2330, 2268	148
Li(η ² -BH ₄)(PMDETA) (see ^c)	2.05(4), 2.04(4) 1.92(4), 1.92(2)	2.29(2) 2.35(2)	1.07(4), 1.07(4) 1.31(4), 1.30(4)	2324, 2284, 2210, 2198, 2181, 2163, 2102	148, 149
NaBH ₄ (15C5)	—	2.70	—	—	150
CpBe(η ² -BH ₄) (see ^a)	1.78(9)	1.88(1)	1.29(5)	2475, 2424, 2170, 1477, 1131, 990, 823	151, 152
(Bu ⁺ O) ₄ Be ₃ (η ² -BH ₄) ₂	1.47(8), 1.63(9)	1.93(1)	1.04(7), 0.89(7)	—	153
Mg(η ² -BH ₄) ₂ (THF) ₃	2.09(4), 1.97(4)	2.451(4)	1.10(4), 1.23(4)	2400, 2370, 2310, 2250, 2090	154
Ca(η ³ -BH ₄) ₂ (DME) ₂	2.474(30), 2.451(29) 2.475(28)	2.646(4)	1.121(34), 1.086(34) 1.085(29)	2370, 2350, 2250, 2210, 2160	155
	2.345(29), 2.429(31) 2.577(29)	2.665(5)	1.135(33), 1.153(29) 1.041(31)		
Ca(η ² -BH ₄) ₂ (η ³ -BH ₄)(Diglyme) ₂ (see ^c)	2.41(4), 2.44(3), 2.60(3) 2.32(3), 2.44(3) 2.41(4), 2.47(4), 2.51(4) 2.38(4), 2.41(4)	2.716(4) (η ³) 2.884(4) (η ²) 2.710(4) (η ³) 2.873(5) (η ²)	1.17(4), 1.11(4), 0.91(5) 1.10(3), 1.15(3) 1.05(4), 1.03(4), 1.06(5) 1.04(5), 0.98(4)	—	156

Table 1 (continued).

Complex	Distance /Å			Vibration frequencies of the BH ₄ group (IR spectroscopy) /cm ^{−1}	Ref.
	M – H _b	M ⋯ B	B – H _b		
Complexes of s-elements and aluminium					
Sr(η ³ -BH ₄) ₂ (Diglyme) ₂	2.64(4), 2.65(4), 2.77(4)	2.916(7)	—	2347, 2247, 2167	157
Sr(η ³ -BH ₄) ₂ (18C6)	2.60(3)	2.833(6)	—	2351, 2297, 2254, 2221, 2164	157
Ba(η ³ -BH ₄) ₂ (Diglyme) ₂	2.69(3), 2.74(4), 2.95(5)	3.058(7)	—	2340, 2274, 2233, 2204, 2153	157
Ba(η ³ -BH ₄) ₂ (18C6)	2.66(4)	2.975(9)	—	2340, 2285, 2237, 2206, 2154	157
Al(η ² -BH ₄) ₃ (see ^b)	1.801(6)	2.143(3)	1.283(12)	2555, 2490, 2218, 2135, 2030, 1930, 1505, 1425, 1112, 605	158 – 160
Al(η ² -BH ₄) ₃					160
α-phase	1.73(4) – 1.76(4)	2.10(2) – 2.14(2)	1.13(4) – 1.14(4)	—	
β-phase	1.67(5) – 1.75(4)	2.10(1) – 2.13(1)	1.12(3) – 1.14(3)	—	
(PMePh ₃)[Al(η ² -BH ₄) ₄]	1.77(4), 1.82(4)	2.261(5),	0.95(5), 1.22(5)	2472, 2411, 2240, 2150, 2127	161
	1.79(5), 1.80(4)	2.229(6)	1.09(5), 1.15(4)		
	1.81(5), 1.83(4)	2.254(7),	1.07(4), 1.11(5)		
	1.77(4), 1.83(5)	2.234(6)	1.04(4), 1.11(5)		
Al(η ² -BH ₄) ₂ Me (see ^b)	1.82(1)	2.152(16)	1.241	2550, 2485, 2035, 1950, 1496, 1414, 1117, 990	162, 163
Al(η ² -BH ₄)Me ₂ (see ^b)	1.77(3)	2.128(8)	1.217(19)	2545, 2475, 2035, 1960, 1540, 1465, 1127, 995	142, 162
Al(η ² -BH ₄) ₃ (NH ₃)	—	2.229(8)	—	—	164
Al(η ² -BH ₄) ₃ (NMe ₃)	1.83(7), 1.75(8)	2.227(11)	1.18(7), 1.40(7)	2515, 2439, 2150	165, 166
	2.00(10), 1.95(11)	2.257(12)	1.16(11), 1.48(10)		
[Al(η ² -BH ₄) ₂ N(CH ₂) ₂] ₂	1.65(4), 1.71(4)	2.193(5)	1.26(5), 1.16(5)	—	167
	1.74(4), 1.84(4)	2.181(5)	1.20(5), 1.22(5)		
[Al(η ² -BH ₄) ₂ (OSiMe ₃)] ₂	—	2.156(5)	—	—	168
		2.143(4)			

Note. The following designations are used: M–H_b is the distance between metal and bridging hydrogen; DMPE is 1,2-bis(dimethylphosphino)ethane; Ph₂Ppy is 1-diphenylphosphinopyridine; DME is 1,2-dimethoxyethane; Cp* is pentamethylcyclopentadienyl; DC18C6 is dicyclohexyl-18-crown-6; Cp is cyclopentadienyl; Ind is indenyl; tritox is tris(*tert*-butyl)methoxy group, Bu₃CO; COT is cyclooctatetraene; BP is methylene-2,2'-bis(4-methyl-6-*tert*-butylphenoxy) group, CH₂(4-Me-6-Bu^tC₆H₂O)₂; 18C6 is 18-crown-6; (COT)^{''} is 1,4-bis(trimethylsilyl)cyclooctatetraene; Ad is adamantyl; NPP is bis[dimethyl(dimethylphosphinomethyl)silyl]amide, N(SiMe₂CH₂PMe₂)₂; DPPM is bis(diphenylphosphino)methane; DMPM is bis(dimethylphosphino)methane; TMEDA is tetramethylethylenediamine; terpy is 2,2':6,2''-terpyridyl; dmphen is 2,9-dimethyl-1,10-phenanthroline; dmdphen is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline; phen is 1,10-phenanthroline; DPPF is 1,1'-bis(diphenylphosphino)ferrocene; Me₈[16]aneS₄ is 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane; Cyclam is 1,4,8,11-tetraazacyclotetradecane; TMAC is 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradecane; 3,5-Me₂pz is 3,5-dimethylpyrazolyl; TG is dimethyl ether of triethylene glycol; py* is *p*-benzylpyridine; coll is 2,4,6-trimethylpyridine (collidine); PMDETA is *N,N,N',N''*-pentamethyldiethylenetriamine; 15C5 is 15-crown-5; Diglyme is diethylene glycol dimethyl ether.

^a Neptunium tetrahydroborate is isomorphous with plutonium tetrahydroborate; their IR spectra in the gas phase are similar to the IR spectrum of hafnium tetrahydroborate (see Ref. 48). ^b Gas phase electron diffraction data. ^c Two independent molecules in the crystal cell. ^d Neutron diffraction data. ^e No structural or spectral data were reported.

Table 2. ¹H NMR and IR-spectroscopic data for some transition metal tetrahydroborates.

Compound	δ(BH _i) /ppm	δ(MH _x B) /ppm	<i>T'</i> /K	<i>T''</i> /K	Δ <i>G</i> [‡] /kcal mol ⁻¹	Vibration frequencies of BH ₄ groups (IR spectroscopy) /cm ⁻¹	Ref.
[Ti(CO) ₄ (η ³ -BH ₄)] ⁺ [K(18C6)] ⁺	0.044	−4.87	178	210	8.8	see ^a	65
Cp ₂ V(η ² -BH ₄)	—	−24	—	185	7.6	2442, 2418, 1745, 1650, 1395, 1180	57
Cp ₂ Nb(η ² -BH ₄)	5.7	−16.5	—	346	14.6	see ^a	169
Cp ₂ ⁺ Nb(η ² -BH ₄)	5.2	−18.2	298	388	16.4	2452, 2428, 1728, 1620, 1171	169
Ind ₂ Nb(η ² -BH ₄)	5.7	−14.2	282	331	13.2	2448, 2412, 2311	170
Cp* CpTa(η ² -BH ₄)	6.27, 5.91	−15.4	298 ^b	> 323	16.4	2478, 2437, 1747, 1621, 1160	171
Ta(η ² -BH ₄)H ₂ (PMe ₃) ₄	4.39	−4.68	193	—	—	2460, 2440, 1980, 1170	172
CrH(η ² -BH ₄)(DMPE) ₂	−29.4	−33.5	—	—	—	see ^a	94
[Mo(CO) ₄ (η ² -BH ₄)](Ph ₃ P) ₂ N]	4.3	−9.8	—	230	10.0	see ^a	96
MoH(η ² -BH ₄)(PMe ₃) ₄	5.5	−4.5	193	—	—	see ^a	97
WH ₃ (η ² -BH ₄)(PMe ₃) ₃	−0.13	−6.25	< 273	—	—	2495, 2420, 2060, 1800, 1275, 1140	94
W(η ² -BH ₄)(CO)(NO)(PPh ₃) ₂	4.0	−2.7, −1.6	193	—	—	2465, 2425	98
W(η ² -BH ₄)(CO)(NO)[P(OPr ₃) ₃] ₂	4.61	−3.71, −2.58	193	—	—	2470, 2430	98
Mn ₂ (CO) ₆ (DPPM)(H)BH ₄	2.9	−14.0	243	310	12.2	2472, 2333	173, 174

Table 2 (continued).

Compound	$\delta(\text{BH}_t)$ /ppm	$\delta(\text{MH}_x\text{B})$ /ppm	T' /K	T'' /K	$\Delta G^\ddagger$ /kcal mol ⁻¹	Vibration frequencies of BH ₄ groups (IR spectroscopy) /cm ⁻¹	Ref.
Mn ₂ (CO) ₅ (DPPM)(H)BH ₄	4.3	−8.6, −12.1 (η^2) −14.6 (η^1)	338 ^b	—	—	2487	174
Mn ₂ (CO) ₆ (TEDIP)(H)BH ₄	—	−15.1	243	—	—	2475, 2360	174
Mn ₂ (CO) ₅ (TEDIP)(H)BH ₄	3.8	−9.5, −12.4 (η^2) −13.45 (η^1)	295 ^b	—	—	2466	174
Re(η^2 -BH ₄)(DPPE) ₂	1.27	−9.0	—	—	—	2400, 2330, 1188	175
ReH(η^1 -BH ₄)(η^2 -BH ₄)(PMe ₂ Ph) ₃	−1.6	−5.3, −13.7	223	—	—	2390, 1100	94
ReH(η^2 -BH ₄)(NO)(PPr ₃) ₂	6.62	−3.91, −6.12	—	—	—	2462, 2437, 1854, 1794	176
ReH(η^2 -BH ₄)(NO)[P(cyclo-C ₆ H ₁₁) ₃]	6.62	−3.59, −6.39	—	—	—	2463, 2437, 1843, 1790	176
ReH(η^2 -BH ₄)(NO)(PPh ₃) ₂	—	−2.92, −4.53	—	—	—	2482, 2446, 1810	176
FeH(η^2 -BH ₄)[MeC(CH ₂ PPh ₂) ₃]	—	−14.7	< 253	> 306	—	see ^a	102, 103
FeH(η^1 -BH ₄)(DMPE) ₂	0.8	−22.4	197 ^b	~240	—	see ^a	123
FeH(η^1 -BH ₄)(DEPE) ₂	—	−21.2	197 ^b	—	—	—	123
FeH(η^1 -BH ₄)(DPrPE) ₂	—	−21	197 ^b	—	—	—	123
Fe ₃ (CO) ₉ H(BH ₄)	3.2	−12.8, −15.8	173	—	—	2335	177
(C ₆ Me ₆) ₂ Ru ₂ H ₃ (BH ₄)	3.2	−13.4	213	—	—	see ^a	178
CpRu(PPh ₃)(η^2 -BH ₄)	—	−17.2	—	—	—	2380	179
Cp*Ru(PMe ₃)(η^2 -BH ₄)	2.14, −3.5	−11.05	303	—	—	2438, 2362, 2282	180
Cp*Ru(PEt ₃)(η^2 -BH ₄)	2.10, −3.22	−11.63	303	—	—	2433, 2352, 2284	180
Cp*Ru(PPr ₃)(η^2 -BH ₄)	—	−12.54	303	—	—	2393, 2318	180
Cp*Ru(PCy ₃)(η^2 -BH ₄)	—	−12.36	303	—	—	2408, 2329	180
Cp*Ru(PPh ₂ Me)(η^2 -BH ₄)	—	−12.0	303	—	—	2387, 2292, 2223	180
Cp*Ru(PPh ₃)(η^2 -BH ₄)	—	−12.03	303	—	—	2450, 2386, 2326	180
RuH(η^2 -BH ₄)(PMe ₃) ₃	6.1–4.5	−6.1 to 79.6	298	< 353	—	2383, 2369, 2318, 1932	104
RuH(η^2 -BH ₄)(PMe ₂ Ph) ₃	5.45	−5.91, −9.08	298	—	—	2402, 2395, 2312	181
RuH(η^2 -BH ₄)(PMePh ₂) ₃	—	−5.1, −9.1	308	—	—	2395, 2375, 2315, 1945, 1370, 1180	182
RuH(η^2 -BH ₄)(PPh ₃) ₃	—	−6.87	—	—	—	2382, 2340, 2080, 1119	183
RuH(η^2 -BH ₄)[PhP(CH ₂) ₃ PPh ₂] ₂	5.1	−5.8, −7.9	300 ^b	348	—	2390, 2380, 2330, 1180	184
RuH(η^2 -BH ₄)[PhP(CH ₂) ₃ PCy ₂] ₂	4.8	−6.8, −9.2	—	—	—	2395, 2330, 1960	185
RuH(η^1 -BH ₄)[P(CH ₂ CH ₂ PPh ₂) ₃]	1.35	−10.28	168	203	—	2360, 2270, 1980, 1052	186
RuH(η^2 -BH ₄)(PP ₃ CyBH ₃)	5.5	−7.0	298	—	—	—	187
RuH(η^2 -BH ₄)(CO)(PPr ₃) ₂	4.55	−4.90, −7.78	233	> 243	—	2420, 2320	188
RuH(η^2 -BH ₄)(CO)(PMeBu ₂) ₂	4.70	−4.40, −7.20	233	> 243	—	2400, 2390	188
[RuH(CO)(PPr ₃) ₂](BH ₄)(BF ₄)	—	−2.85 (2H) −5.76 (2H)	223	> 243	—	—	189
RuH(η^1 -BH ₄)(PNP)(PPh ₃)	2.5	−8.9	193	—	—	2360, 2322, 1915, 1845, 1058	190
RuH(η^2 -BH ₄)(<i>S</i> -biphemp)(PPh ₃)	5.8	−4.0, −9.1	293	373	—	2403, 2380, 2333, 1966, 1331, 1178	191
OsH ₃ (η^2 -BH ₄)(PPr ₃) ₂	8.78 8.79	−6.78 −10.14	213 360	300(H _b –OsH), 13.2 > 360(H _b –H _t) > 20	—	2447, 2351	10, 192
OsH ₃ (η^2 -BH ₄)[P(cyclo-C ₅ H ₉) ₃] ₂	9.05 8.8	−6.83 −10.19 ^b	193 363	—	—	see ^a	105
OsH(η^2 -BH ₄)(CO)(PPr ₃) ₂	6.10	−6.50, −8.10	233	> 243	—	2430, 2330	188
OsH(η^2 -BH ₄)(CO)(PMeBu ₂) ₂	6.35	−6.15, −7.75	233	> 243	—	2440, 2420	188
[OsH(CO)(PPr ₃) ₂](BH ₄)(BF ₄)	—	−3.82 (2H) −5.39 (2H)	223	> 243	—	—	189
Co(η^2 -BH ₄)terpy	1.73	−9.97	213	> 254	11.1	see ^a	193
Rh(η^2 -BH ₄)H ₂ (PMeBu ₂) ₂	3.9	−4.53	300	—	—	—	194
Ir(η^2 -BH ₄)H ₂ (PMeBu ₂) ₂	6.86	−6.86	300 ^b	> 300	—	2458, 2347, 2150, 1308, 1188	195
Ir(η^2 -BH ₄)H ₂ (PBu ₃) ₂	6.17	−7.76	300 ^b	> 300	—	2460, 2367, 2142, 1330, 1196	195
Cp ₂ Ir ₂ H ₃ (BH ₄)	5.5	−14.2	298	—	—	see ^a	196

Note. The following designations are used: $\delta(\text{BH}_t)$ and $\delta(\text{MH}_x\text{B})$ refer to the signals of the terminal and bridging hydrogen atoms of the tetrahydroborate ligands, respectively; T' is the temperature at which the spectrum was recorded; T'' is the temperature of coalescence of signals of bridging and terminal protons; $\Delta G^\ddagger$ is the activation energy for the exchange of bridging and terminal protons; TEDIP is tetraethyl pyrophosphite; DPPE is 1,2-bis(diphenylphosphino)ethane; DEPE is 1,2-bis(diethylphosphino)ethane; DPrPE is 1,2-bis(dipropylphosphino)ethane; PP₃Cy is tris(dicyclohexylphosphinoethyl)phosphine, P[CH₂CH₂P(cyclo-C₆H₁₁)₂]₃; PNP is 1,2-bis[*N,N*-bis(2-diphenylphosphinoethyl)amino]ethane; *S*-biphemp is (*S*)-2,2'-dimethyl-6,6'-bis(diphenylphosphino)biphenyl.

^a The data of IR spectroscopy are presented in Table 1. ^b The spectrum was recorded under the ¹H–{¹B} double resonance conditions.

mono-, bi- and tridentate terminal BH₄ groups (Fig. 1) and polynuclear complexes with diverse tetrahydroborate bridges between metal atoms (Fig. 2).

If the positions of hydrogen atoms cannot be determined by X-ray diffraction analysis, the denticity of the BH₄ ligand can be estimated from the metal–boron distance. These distances in

Table 3. Polynuclear complexes with bridging tetrahydroborate groups.

Compound	Type of coordination of the BH ₄ group according to X-ray diffraction data	See Fig. 2	Vibration frequencies of the BH ₄ groups (IR spectroscopy) /cm ⁻¹	Ref.
LiBH ₄ (Et ₂ O)	{(Et ₂ O)Li[(μ ₂ -H)(μ ₂ '-H)(μ ₂ ''-H)(μ ₄ -H)B]} _∞	<i>c</i>	2364, 2286, 2234, 2230	147, 197
LiBH ₄ (MeOBu ^t)	{(MeOBu ^t)Li[(μ ₂ -H)(μ ₂ '-H)(μ ₃ -H)(μ ₃ '-H)B]} _∞	<i>d</i>	2410, 2320, 2306, 2277, 2180	147
LiBH ₄ (C ₃ H ₆ O ₂)	{(C ₃ H ₆ O ₂)Li[(μ ₂ -H) ₂ (μ ₂ '-H) ₂ B]} _∞	<i>a</i>	2317, 2256, 2180	147
LiBH ₄ (TMEDA)	{(TMEDA)Li[(μ ₂ -H)(μ ₂ '-H)(μ ₃ -H)BH]} ₂	<i>b</i>	—	198
LiBH ₄ (TMTA)	{(TMTA)Li[(μ ₂ -H)(μ ₂ '-H)(μ ₃ -H)BH]} ₂	<i>b</i>	2367, 2343, 2271, 2225, 2154	148
[H ₂ C(3,5-Me ₂ pz) ₂ LiBH ₄	{[H ₂ C(3,5-Me ₂ pz) ₂ Li[(μ ₂ -H)(μ ₂ '-H)(μ ₃ -H)BH]} ₂	<i>b</i>	2376, 2332, 2292, 2259, 2241, 2221, 2181, 2168, 2138	145
(4,4'-Me ₂ bipy)LiBH ₄	{(4,4'-Me ₂ bipy)Li[(μ ₂ -H)(μ ₂ '-H)(μ ₃ -H)BH]} ₂	<i>b</i>	2390, 2293, 2227	145
NaBH ₄ (Diglyme)	{(Diglyme)Na[(μ ₂ -H)(μ ₂ '-H)(μ ₃ -H)BH]} _∞	<i>b</i>	—	199
NaBH ₄ (PMDETA)	{(PMDETA)Na[(μ ₂ -H)(μ ₃ -H) ₂ BH]} ₂	<i>j</i>	2316, 2249, 2184	148
NaBH ₄ (TMTCN)	{(TMTCN)Na[(μ ₄ -H)BH ₃]} ₄	<i>h</i>	2398, 2304, 2227	148
Be(BH ₄) ₂	{Be(η ² -BH ₄)[(μ ₂ -H) ₂ (μ ₂ '-H) ₂ B]} _∞	<i>a</i>	2510, 2451, 2330, 2113, 2075, 1995	200, 201
Sr(BH ₄) ₂ (THF) ₂	{(THF) ₂ Sr[(μ ₂ -H)(μ ₂ '-H)(μ ₃ -H) ₂ B]} _∞	<i>i</i>	2372, 2313	157
Ba(BH ₄) ₂ (THF) ₂	{(THF) ₂ Ba[(μ ₂ -H)(μ ₂ '-H)(μ ₃ -H) ₂ B]} _∞	<i>i</i>	2353, 2308, 2241, 2216, 2186, 2169	157
Me ₂ AlBH ₄	{Me ₂ Al[(μ ₂ -H) ₂ (μ ₂ '-H) ₂ B]} _∞	<i>a</i>	—	160
Y(BH ₄) ₃ (DME)	{(DME)Y(η ³ -BH ₄) ₂ [(μ ₂ -H) ₂ (μ ₂ '-H) ₂ B]} _∞	<i>a</i>	2468, 2319, 2300, 2230, 2175	202
(1,3-Bu ⁱ ₂ C ₅ H ₃) ₂ CeBH ₄	{(1,3-Bu ⁱ ₂ C ₅ H ₃) ₂ Ce[(μ ₂ -H)(μ ₂ '-H)(μ ₃ -H) ₂ B]} ₂	<i>i</i>	2290, 2180, 2100	203
(1,3-Bu ⁱ ₂ C ₅ H ₃) ₂ SmBH ₄	{(1,3-Bu ⁱ ₂ C ₅ H ₃) ₂ Sm[(μ ₂ -H)(μ ₂ '-H)(μ ₃ -H) ₂ B]} ₂	<i>i</i>	2420, 2280	204
(COT)(THF) ₂ NdBH ₄	{(COT)(THF) ₂ Nd[(μ ₂ -H)(μ ₂ '-H)(μ ₃ -H) ₂ B]} ₂	<i>i</i>	2255	205
ansa-Cp ₂ 'Yb(BH ₄) ₂ Li(THF) ₂	{ansa-Cp ₂ 'Yb[(μ ₂ -H) ₂ (μ ₂ '-H) ₂ B][(μ ₂ -H) ₂ (μ ₂ ''-H) ₂ B]Li(THF) ₂ } _∞	<i>a</i>	—	206
U(BH ₄) ₄	{U(η ³ -BH ₄) ₂ [(μ ₂ -H) ₂ (μ ₂ '-H) ₂ B]} _∞	<i>a</i>	2552, 2538, 2262, 2182, 2087	207–210
U(BH ₄) ₄ (OMe) ₂	{(MeO)U(η ³ -BH ₄) ₃ [(μ ₂ -H) ₂ (μ ₂ '-H) ₂ B]} _∞	<i>a</i>	—	211
U(BH ₄) ₄ (OEt) ₂	{(EtO)U(η ³ -BH ₄) ₃ [(μ ₂ -H) ₂ (μ ₂ '-H) ₂ B]} _∞	<i>a</i>	—	211
U(BH ₄) ₄ (OPr) ₂	{(PrO)U(η ³ -BH ₄) ₃ [(μ ₂ -H) ₂ (μ ₂ '-H) ₂ B]U'(η ³ -BH ₄) ₄ }	<i>a</i>	—	212
[Cr ₂ (Pr ⁱ NCHNPr ⁱ) ₃]BH ₄	[Cr ₂ (Pr ⁱ NCHNPr ⁱ) ₃][(μ ₂ -H)(μ ₂ '-H) ₂ BH ₂]	<i>f</i>	2401, 2365, 2236, 2101	93
Cr ₃ (BH ₄) ₆ (TMEDA) ₂ Py ₄	[(TMEDA)PyCr(η ² -BH ₄)[(μ ₂ -H)(μ ₂ '-H)BH ₂] ₂ [Py ₂ Cr'(η ² -BH ₄) ₂]	<i>f</i>	—	93
Mn ₂ (CO) ₆ (DPPM)(H)BH ₄	[Mn(CO) ₃] ₂ (μ ₂ -DPPM)(μ ₂ -H)[(μ ₂ -H)(μ ₂ '-H)BH ₂]	<i>f</i>	2472, 2333	173
Mn ₂ (CO) ₅ (DPPM)(H)BH ₄	[Mn(CO) ₃](μ ₂ -DPPM)(μ ₂ -H)[(μ ₂ -H)(μ ₂ '-H) ₂ BH][Mn'(CO) ₂]	<i>e</i>	2487	174
HfFe ₃ (CO) ₉ (BH ₄)	H[Fe(CO) ₃] ₃ [(μ ₂ -H)(μ ₂ '-H)(μ ₂ ''-H)BH]	<i>g</i>	2335	177
[RuH(CO)(PPR ₃ ⁱ) ₂] ₂ (BH ₄)(BF ₄)	[RuH(CO)(PPR ₃ ⁱ) ₂] ₂ [(μ ₂ -H) ₂ (μ ₂ '-H) ₂ B](BF ₄)	<i>a</i>	—	189
[OsH(CO)(PPR ₃ ⁱ) ₂] ₂ (BH ₄)(BF ₄)	[OsH(CO)(PPR ₃ ⁱ) ₂] ₂ [(μ ₂ -H) ₂ (μ ₂ '-H) ₂ B](BF ₄)	<i>a</i>	—	189
[HC(CH ₂ PPh ₂) ₃ RuH] ₂ (BH ₄)(BPh ₄)	[HC(CH ₂ PPh ₂) ₃ RuH] ₂ [(μ ₂ -H) ₂ (μ ₂ '-H) ₂ B](BPh ₄)	<i>a</i>	—	213
(C ₆ Me ₆) ₂ Ru ₂ H ₃ (BH ₄)	[(C ₆ Me ₆)RuH ₂](μ ₂ -H)[(μ ₂ -H)(μ ₂ '-H)BH ₂]	<i>f</i>	2355, 2220	178
Co(DPPP)(BH ₄)	{(DPPP)Co[(μ ₂ -H)(μ ₂ '-H)(μ ₃ -H)BH]} ₂	<i>b</i>	2415, 2030, 1985	214
Cp [*] Ir ₂ H ₃ (BH ₄)	[(Cp [*] IrH) ₂ (μ ₂ -H)][(μ ₂ -H)(μ ₂ '-H)BH ₂]	<i>f</i>	2430, 2360, 2290, 2115, 2040	196
{[(Ph ₃ P) ₂ Cu] ₂ BH ₄ }ClO ₄	[(Ph ₃ P) ₂ Cu] ₂ [(μ ₂ -H) ₂ (μ ₂ '-H) ₂ B]ClO ₄	<i>a</i>	2190, 2140, 2050	215, 216
MeZnBH ₄	{MeZn[(μ ₂ -H) ₂ (μ ₂ '-H) ₂ B]} _∞	<i>a</i>	2255, 2215	217, 218
[cyclo-(<i>o</i> -C ₆ F ₄ Hg) ₃](BH ₄) ₂ (Bu ₄ N) ₂	—	—	2300, 2035	219, 220
[cyclo-(<i>o</i> -C ₆ F ₄ Hg) ₃] ₂ (BH ₄)(Bu ₄ N)	—	—	2159, 2052	219, 220
GaH ₂ (BH ₄)	{GaH ₂ [(μ ₂ -H) ₂ (μ ₂ '-H)BH](Ga'H ₂)(μ ₂ -H) ₂ (μ ₂ ''-H)BH ₂ } · (Ga''H ₂ [(μ ₂ '-H)(μ ₂ ''-H) ₂ BH]} _∞	<i>e, f</i>	—	221

Note. The following designations are used: TMTA is trimethylhexahydrothiazine; bipy is bipyridine; TMTCN is 1,4,7-trimethyltriazacyclononane; *ansa*-Cp' is methylenebis(3-trimethylsilylcyclopentadienyl), CH₂(Me₃SiC₅H₃)₂; DPPP is 1,5-bis(diphenylphosphino)pentane, Ph₂P(CH₂)₅PPh₂.

tetrahydroborate complexes are usually close to the sum of the Shannon ion radius of the metal²²² and the radius of the BH₄

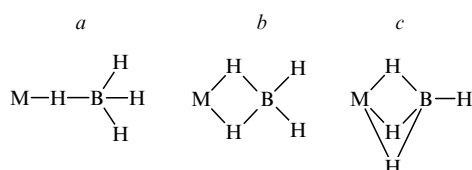


Figure 1. Coordination of terminal tetrahydroborate ligands in covalent complexes;

(a) monodentate η¹; (b) bidentate η²; (c) tridentate η³.

ligand with the corresponding denticity [for η³-BH₄, $r_i \approx 1.36(6) \text{ \AA}$ and for η²-BH₄, $r_i \approx 1.6(1) \text{ \AA}$].²²³ In most cases, the results of this summation are in good agreement with experimental results. For example, for La(III) with a coordination number of 12 ($r_i = 1.36 \text{ \AA}$),²²² the lanthanum–boron distances calculated in this way (2.72 and 2.96 Å) are close to the values found experimentally (2.76 and 2.90 Å) in [La(η²-BH₄)₂(η³-BH₄)₂(THF)₂][–] (see Ref. 18). However, when the coordination number is low and the complex contains bulky ligands, the calculated metal–boron distances deviate substantially from those found experimentally. In our opinion, these deviations point to a considerable influence of steric factors on the structural properties of the BH₄ ligands in the complexes. The use of so-

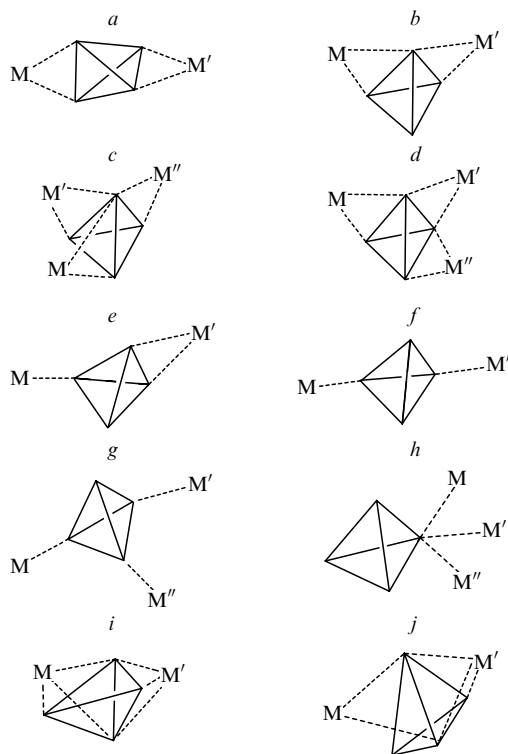


Figure 2. Coordination of bridging tetrahydroborate ligands in polynuclear complexes; (a–j) see the text.

called effective coordination numbers, instead of the true values, has been proposed for compounds of this type.²²³

Valuable information concerning the type of the metal–ligand bond in the compounds under consideration can be gained using vibrational (IR and Raman) spectroscopy.^{2,3} The observed absorption bands of BH_4 ligands with different denticities were assigned resorting to the studies of model compounds with known structures. Certain correlations between the spectral characteristics and structures of complexes were established. The most characteristic spectral region for the compounds in question is the region of stretching vibrations of the B–H bonds ($\sim 1650\text{--}2600\text{ cm}^{-1}$). As a rule, a tridentate BH_4 group is responsible for an intense absorption band at $\sim 2450\text{--}2600\text{ cm}^{-1}$ [stretching vibrations of the terminal B–H bonds, $\nu(\text{B-H}_t)$] and for an intense doublet of bands at about $2100\text{--}2200\text{ cm}^{-1}$ [stretching vibrations of the B–H bridging bonds, $\nu(\text{B-H}_b)$]. A bidentate type of coordination shows itself as an intense doublet of bands in the region of $2400\text{--}2600\text{ cm}^{-1}$ and an intense band (perhaps, with a shoulder) at $\sim 1650\text{--}2150\text{ cm}^{-1}$. Monodentate complexes are characterised by two broadened absorption bands, $\sim 2300\text{--}2450$ and $\sim 2000\text{ cm}^{-1}$ (see Refs 2–5). Complexes in which the BH_4 group is bound to the metal ion *via* one or several M–H–B bonds have been named covalent tetrahydroborates.²

Unlike X-ray diffraction and IR spectroscopy data, the data of NMR spectroscopy for many tetrahydroborate complexes, both ionic and covalent, point to the equivalence of the four protons in the BH_4 ligand. The disagreement between the results obtained by different methods is due to the difference between the time scales of X-ray diffraction analysis and IR spectroscopy (characteristic time $\sim 10^{-18}\text{--}10^{-20}\text{ s}$), on the one hand, and NMR (characteristic time $\sim 10^{-2}\text{--}10^{-9}\text{ s}$), on the other hand, and to the fluxionality of these compounds on the NMR time scale, *i.e.*, the ability of the bridging and terminal protons of tetrahydroborate ligands to undergo fast intramolecular exchange.^{2–5}

In terms of composition, tetrahydroborate complexes can be divided into two groups, homoleptic (containing one type of ligand) and heteroleptic (containing different ligands). Analysis of the vast experimental information accumulated to date permits one to establish the main types of tetrahydroborate complexes formed commonly by metals of each Group. Neutral homoleptic tetrahydroborates $\text{M}''(\text{BH}_4)_n$ are typical of alkali and alkaline earth metals, beryllium, magnesium and aluminium. Among transition and post-transition metals, these complexes are known only for some lanthanides in the oxidation states +2 or +3, titanium subgroup metals, some actinides, zinc, cadmium and thallium(I).^{1–5,224} Many neutral tetrahydroborates are able to attach additional BH_4 groups to give anionic complexes of the type $[\text{M}''(\text{BH}_4)_{n+k}]^{k-}$ ($k = 1\text{--}3$); however, this anion stabilises noticeably only tetrahydroborates of 3d metals of the beginning of the transition metal row, from Sc to Fe. No homoleptic anionic complexes of cobalt, nickel, copper or Group I and V–VIII 4d or 5d transition metals have been obtained in a pure state.²²⁵

In most cases, in addition to BH_4 groups, tetrahydroborate complexes contain various stabilising ligands; the ligands found most often are ethers and polyethers, amines and polyamines (both cyclic and acyclic), cyclopentadienide anion derivatives and compounds of trivalent phosphorus (tertiary organic phosphines and phosphites). A large number of relatively stable complexes with ethers have been prepared for elements for which non-solvated neutral tetrahydroborates are known. A complex with tetrahydrofuran stable at room temperature is also formed by divalent manganese the ions of which possess a half-filled *d* shell.⁹⁹ For other transition metals, these complexes are either unstable [for example, the chromium complex $\text{Cr}(\text{BH}_4)_2(\text{THF})_2$ decomposes at -20°C] or unknown.³

Complexes with ligands such as halide, alkoxy or aryloxy anions and NO are rather rarely encountered in the chemistry of tetrahydroborates. Complexes with CO molecules as ligands are quite numerous but are mainly formed for Group VI–VIII metals. Anionic ligands (amides, alkoxides, aryloxides, *etc.*) stabilise effectively only tetrahydroborates formed by 3d metals of the beginning of the transition metal row. Examples of stabilisation of platinum metal complexes by cyclopentadienyl ligands are also documented. Unlike the above-mentioned ligands, amines and polyamines stabilise more efficiently complexes of metals from the middle to the end of each transition metal row.

Organic tertiary phosphines are the most efficient stabilising ligands for tetrahydroborates. In many cases, complexes contain hydride ligands together with phosphines. Tetrahydroborate complexes with these ligands are known for most transition metals but not for rare earth elements. The broad range of stabilising capacity of phosphines is stipulated by the broad range of variation of steric and electronic properties of these compounds. To fill the valence shells of metal atoms of the beginning of a transition metal row, a large number of electron-donating ligands are needed; in this case, strong electron donors having relatively small sizes such as trimethylphosphine and bis(dimethylphosphino)ethane are effective. On the contrary, to stabilise Group VIII metal complexes, a few ligands should shield the central atom having many valence electrons from contacts with the outer-sphere electron acceptors. In this case, the stability of complexes increases when they contain bulky ligands $[\text{P}(\text{cyclo-C}_6\text{H}_{11})_3, \text{PBu}_3]$.

The most diverse types of tetrahydroborate complexes are formed by Group I, III and IV transition metals, although no complexes with CO ligands have been found for Group III metals and no complexes with CO or Cp ligands have been described for Group I transition metals. The tetrahydroborate complexes of nickel and palladium are least diverse (no complexes of this type are known for platinum), which is in sharp contrast with the extremely varied chemistry of coordination compounds of these metals with many other ligands (Ni, Pd, Pt are typical complex-forming elements). The typical stabilising ligands vary depending on the position of the metal in the Periodic Table. Whereas for

Table 4. The ability of ligands of different types to stabilise transition metal tetrahydroborates.

M	$M^n(\text{BH}_4)_n$	$[\text{M}^n(\text{BH}_4)_{n+1}]^-$	L in the complexes $\text{M}(\text{BH}_4)_n\text{L}_x$							Other ligands
			ethers	NR_2^-	Cp derivatives	CO	amines	H	PR_3	
REE	+	+	+	—	+	—	+ (Ln^{II})	—	—	+
Actinides	+	+	+	+	+	—	+ (U)	+	+	+
Ti, Zr, Hf	+	+	+	+	+	+ (Ti)	+	+	+	+
V, Nb, Ta	—	+ (V)	—	+ (V)	+	+ (Ta)	—	+	+	+
Cr, Mo, W	—	+ (Cr)	+ (Cr)	+ (Cr)	—	+	+ (Cr)	+	+	+
Mn, Re	—	+ (Mn)	+ (Mn)	—	—	+	+ (Mn)	+	+	+
Fe, Ru, Os	—	+ (Fe)	—	—	+ (Ru)	+	+	+	+	+
Co, Rh, Ir	—	—	—	—	+ (Ir)	+ (Rh, Ir)	+ (Co)	+	+	+
Ni, Pd	—	—	—	—	—	—	+ (Ni)	+	+	+
Cu, Ag	—	—	—	—	—	—	+ (Cu)	—	+	+
Pt, Au	—	—	—	—	—	—	—	—	—	—
Zn, Cd	+	+	+	—	—	—	+	+	—	+
Hg	—	—	—	—	—	—	—	—	—	+

Note. A plus sign means that for the given group of metals, tetrahydroborate complexes with ligands of this particular type are known, while a minus sign means that these complexes are unknown; the metal (or ion) to which the plus sign refers is given in parentheses.

complexes of Group III and IV transition metals, ethers and amines are commonly found ligands, in the case of Group I and V–VIII metal tetrahydroborates, compounds with these ligands are unusual. The ligands found most often for the latter type of metals are derivatives of tertiary organic phosphines, which are represented by only a few examples in the case of Group III and IV transition metal complexes.

The dependence of the types of stabilising ligands and complexes they form on the nature of the central transition metal atom can be followed by analysing the data of Table 4. It can be seen that the number of ligand types capable of efficient stabilisation of tetrahydroborate complexes decreases on passing from Group III and IV transition metals to Group VIII metals, especially to nickel and palladium for which only few examples of tetrahydroborate complexes are known. The decrease in the stability of tetrahydroborate complexes is even more pronounced on passing from 3d to 4d and 5d metals. As a result of these two trends, no tetrahydroborate complexes of 5d metals of the end of the transition row, *viz.*, platinum or gold, have been characterised.

III. Transition metal complexes with terminal BH_4 ligands

The complexes of Group III and IV transition metals are most diverse regarding the mode of addition of the BH_4 ligands to the central atom (see Table 1). Compounds with any of the main types of coordination (see Fig. 1) can be found among complexes of these metals. Molecules containing BH_4 ligands coordinated to the same metal atom in two different modes are also known, for example, $\text{Sc}(\eta^2\text{-BH}_4)(\eta^3\text{-BH}_4)_2(\text{THF})_2$,¹¹ $\text{Y}(\eta^2\text{-BH}_4)(\eta^3\text{-BH}_4)_2\cdot(\text{THF})_3$,¹⁴ $(\text{BP})\text{Zr}(\eta^3\text{-BH}_4)(\eta^2\text{-BH}_4)\cdot(\text{THF})$.⁶⁴ The $\text{Hf}_2\cdot(\text{NPP})_2\text{H}_2(\text{BH}_4)_3$ complex contains simultaneously mono-, bi- and tridentate BH_4 groups.⁸³

The structures of Group I and V–VIII metal complexes are much less studied (see Table 1); this can be explained by the sensitivity of many of them to oxygen and moisture and thermal instability and the difficulty of their synthesis and investigation arising thereupon. The structural chemistry of the tetrahydroborates of Group I and V–VIII transition metals is much scantier than that for Group III and IV metals. No complexes with tridentate BH_4 groups have been found for them; in the majority of their compounds, the BH_4 groups are bidentate ligands.

Among compounds of Group I and V–VIII transition metals, there are quite a few complexes with a monodentate coordination of tetrahydroborate ligands ($\sim 25\%$ of the total number of structurally characterised complexes of the metals in question); this type of coordination is rather poorly studied. Nowadays, the

existence of complexes with $\eta^1\text{-BH}_4$ groups has been reliably established by X-ray diffraction analysis and neutron diffraction. Structures of about 10 compounds of this type determined by X-ray diffraction analysis are documented; one of these compounds has also been studied by neutron diffraction. Taking into account the data of NMR spectroscopy, we would like to note that for Group I and IV–VIII transition metals, at least one example of an η^1 -complex can be given for each group.

It is noteworthy that all η^1 -complexes incorporate P-, N- or S-donor ligands (tertiary organic phosphines, amines and thia- and aza-macrocycles) possessing strong electron-donating properties. In most of these compounds, the central atom is linked to three or more phosphorus, nitrogen, or sulfur atoms.

In terms of the type of the stabilising ligand, the compounds considered can be divided into two groups, namely, complexes with P- and N-donor ligands, which differ markedly in physico-chemical characteristics. The length of the $\text{M}-\text{H}_b$ bond in the former type of compound varies from 1.60 to 1.88 Å and the $\text{M}-\text{B}$ distance ranges from 2.44 to 2.84 Å. The $\text{M}-\text{H}-\text{B}$ bond is bent, the MHB angle ranging from 121 to 164°. The IR spectra of these compounds exhibit broad absorption bands in the ranges of 2300–2350 cm^{-1} [$\nu(\text{BH}_t)$] and $\sim 2000\text{--}2100\text{ cm}^{-1}$ [$\nu(\text{BH}_b)$], which is consistent with the values predicted for η^1 -complexes.³ Resorting to the above-mentioned correlation between the structures and spectroscopic properties, the presence of monodentate BH_4 groups in L_3CuBH_4 type complexes [$\text{L} = \text{P}(\text{HPh})_2$, $\text{P}(\text{OPr}^i)_2\text{Ph}$, $\text{P}(\text{Me}_2\text{Ph})$] was demonstrated by IR spectroscopy. Study of the relationship between the structure of the copper compounds L_nCuBH_4 and the electronic and steric properties of phosphine ligands L showed that the complexes $\text{L}_3\text{Cu}(\eta^1\text{-BH}_4)$ with monodentate tetrahydroborate ligands are formed only when the electron-donating ligands L have a moderate size. A decrease in the electron-donating ability of the ligands, as well as an increase in their size, result in the complexes $\text{L}_2\text{Cu}(\eta^2\text{-BH}_4)$.¹¹⁸

However, compounds with N-donor ligands follow a different type of regularities. X-ray diffraction data point to an unusually long metal–boron distance (3.09–3.31 Å) in these compounds and IR spectra attest to the presence of BH_4^- anions.^{130,131} In solutions, these complexes appear to have ionic structure.¹³²

For compounds with P-donor ligands, the difference between the experimentally determined metal–boron distance and the ion radius of the central atom is 2.0 ± 0.2 Å. In the complexes with N-donors, this difference is close to 2.4 Å, *i.e.* it substantially exceeds the radius of the BH_4^- anion (2.04 Å). This long metal–boron distance implies apparently the absence of covalent interaction between the central atom and the ligand, the monodentate

coordination of the BH_4 ligand in the crystals of these compounds being related to packing effects.

The NMR spectra of some monodentate complexes exhibit separate signals for the terminal and bridging protons, *i.e.* these compounds are less fluxional than complexes with tridentate BH_4 groups. It was shown in relation to iron compounds that an increase in the size of stabilising ligands increases the stereochemical rigidity of complexes, *i.e.* stabilises the η^1 -coordination.¹²³ However, comparison of the structures of $\text{Ti}(\eta^2\text{-BH}_4)_2\text{.(DMPE)}_2$ (d^2 -configuration of titanium) with $\text{V}(\eta^1\text{-BH}_4)_2\text{.(DMPE)}_2$ (d^3 -configuration of vanadium)^{53,54} and $\text{CrH}(\eta^2\text{-BH}_4)(\text{DMPE})_2$ (d^4 -configuration of chromium) with $\text{FeH}(\eta^1\text{-BH}_4)(\text{DMPE})_2$ (d^6 -configuration of iron),^{94,123} which contain Ti(II) or V(II) and Cr(II) or Fe(II) ions with closely similar radii, demonstrates that η^1 -coordination is not determined by steric factors alone. The η^1 -coordination may also be facilitated by the d^3 -configuration of V(II) and the d^6 -configuration of Fe(II) , which are favourable for the formation of octahedral complexes. The tetrahedral geometry, preferred for d^{10} ions for energy reasons, stipulates apparently the formation of the monodentate complexes $\text{Cu}(\eta^1\text{-BH}_4)(\text{PMePh}_2)_3$ and $\text{Ag}(\eta^1\text{-BH}_4)(\text{PMePh}_2)_3$, despite the fact that the ionic radius of Ag(I) is greater than that of Cu(I) and the volume of the silver coordination sphere is sufficient for η^2 -coordination.^{125,129} A η^1 -coordination of BH_4 has been suggested previously for $\text{RuH}(\eta^2\text{-BH}_4)(\text{PPh}_3)_3$,¹⁸³ however, the fact that its IR spectrum differs from the IR spectra typical of η^1 -complexes and resembles the spectrum of the complex $\text{RuH}(\eta^2\text{-BH}_4)(\text{PMe}_3)_3$, which has been characterised by X-ray diffraction analysis (see Table 1), points to a bidentate coordination of the BH_4 group in this complex.

Thus, in all the known cases, monodentate coordination of the BH_4 groups is due to the presence of stabilising ligands possessing definite properties (strong electron donors having a large size), *i.e.* this type of coordination is forced. Complexes with η^1 -coordination of BH_4 groups might also be possible for ions with a different electron configuration provided that the coordination sphere contains a sufficient number of bulky electron-donating ligands. However, the currently available data do not allow one to predict unambiguously the appearance of η^1 -coordination in each particular case.

The IR spectroscopic studies show that in most cases, experimental results are in good agreement with those predicted theoretically for the BH_4 groups of the corresponding coordination;^{2–5} however, in some cases, the absorption bands due to the stretching vibrations of terminal B–H bonds occur at a substantially lower frequency than expected (see Tables 1, 2). Experimental data on the structures of tetrahydroborate complexes show that the idea of the three main types of coordination of the BH_4 ligands in so-called covalent tetrahydroborates is an idealisation. Among complexes of both Group III, IV and Group I, V–VIII transition metals, there are compounds with a distorted geometry of coordinated BH_4 ligands (unequal M–H_b distances and MH_bB angles), which hampers unambiguous identification of the type of coordination. For example, in the structure of $\text{Ti}(\eta^2\text{-BH}_4)(\eta^3\text{-BH}_4)_2(\text{PMe}_3)_2$, the tridentate coordination of the two BH_4 ligands is so distorted that these groups can be regarded as being coordinated through the B–H bonds (the Ti–B distance is 2.27 Å, Ti–H_b is 1.73 Å, the MH_bB angle is 112°).⁵²

It has been noted that this coordination can be regarded as being characteristic of a hypothetical transition state in the activation of the methane molecule, isoelectronic with the tetrahydroborate anion. A similar distortion of a symmetrical coordination is also observed for some η^2 -complexes, for example, for $(\text{phen})(\text{PPh}_3)\text{Cu}(\eta^2\text{-BH}_4)$ (the Cu–B distance is 2.29 Å, Cu–H_b is 1.63 Å).¹¹⁴ This type of coordination plays, apparently, an important role in the exchange of bridging hydrogen atoms and hydride ligands in the complexes $\text{MH}_3(\text{BH}_4)\text{L}_2$.¹⁰ It has been noted above that the M–H_b–B bridge in monodentate complexes is bent, and the MH_bB angle varies over wide limits (from 120 to 164°); hence, in some cases [for example, in

$\text{Hf}_2(\text{NPP})_2\text{H}_2(\eta^3, \eta^2, \eta^1\text{-BH}_4)_3$], the coordination of BH_4 groups found experimentally can be considered to be intermediate between mono- and bidentate coordinations.⁸³ The distortion of the geometry of coordinated ligands affects substantially the spectral properties of the complexes; therefore, in some cases, the denticity of the BH_4 groups cannot be identified unambiguously from the data of vibrational spectroscopy; for example, this is true for the copper and titanium compounds considered above.^{52,114}

Compounds of Group III and IV transition metals possess clear-cut fluxionality; therefore, all the protons of the BH_4 ligands are equivalent on the NMR time scale.^{2–5} Until recently, for none of the complexes of this type, were separate signals for the terminal and bridging protons of tetrahydroborate ligands distinguished in the NMR spectra, not even at low temperatures (for some compounds, studies were performed at ~150 K).³ The activation energy for the exchange of terminal and bridging protons in these compounds equals ~5 kcal mol^{–1}, as estimated for $\text{Cp}_3\text{U}(\eta^3\text{-BH}_4)$.³ For compounds of Group IB metals, separate signals for bridging and terminal protons have not been identified either.²²⁶ Only recently, was the first titanium compound reported [the complex $[\text{Ti}(\text{CO})_4(\eta^3\text{-BH}_4)]^-[K(18\text{C}6)]^+$] for which the limit of slow proton exchange was attained at 178 K and individual signals for the terminal and bridging protons of $\eta^3\text{-BH}_4$ were observed.⁶⁵ The fact that the tetrahedral geometry of the BH_4^- anion in this complex is virtually non-distorted indicates a low contribution of the covalent constituent to the interaction of the central atom with this ligand. Note that in the analogous chromium and molybdenum complexes $[\text{M}(\text{CO})_4(\eta^2\text{-BH}_4)]^-$, the tetrahydroborate ligand has a bidentate coordination. The unique structural and dynamic properties of the titanium complex (this is the only example of a tridentate tetrahydroborate group for which individual signals from the terminal and bridging protons were observed) are apparently due to the combination of the carbonyl groups (active π -acceptors and the most 'powerful' strong-field ligands) with an 'early' 3d metal in a low oxidation state in one molecule.

Many tetrahydroborates of Group V–VIII metals are much less fluxional than complexes formed by Group III and IV transition metals (see Table 2). At low temperature, individual signals of the terminal and bridging protons for both η^2 - and $\eta^1\text{-BH}_4$ groups can be distinguished in the NMR spectra of these compounds. It is of interest that in some cases, bridging protons of the $\eta^2\text{-BH}_4$ groups account for two separate signals and the exchange of these non-equivalent bridging protons with terminal protons occurs at different rates.¹⁷¹ In some complexes, this proton exchange does not proceed at a noticeable rate even at room temperature, or at higher temperatures. Thus for one of the least fluxional tetrahydroborates $\text{Os}(\eta^2\text{-BH}_4)\text{H}_3(\text{PPR}_3)_2$, this process cannot be observed even at 360 K. The activation energy for the exchange of the terminal and bridging protons in this compound cannot be determined experimentally because this compound decomposes at higher temperatures. According to estimates,¹⁰ this energy is greater than 20 kcal mol^{–1}. At 300 K, the bridging protons in this compound undergo fast exchange with the hydride ligands ($\text{Os})\text{H}_3$ (activation energy ~13 kcal mol^{–1}). The results of experimental studies and quantum-chemical calculations for $\text{Os}(\eta^2\text{-BH}_4)\text{H}_3(\text{PPR}_3)_2$ provide grounds for suggesting that the exchange of bridging hydrogen atoms (B)H_b with the hydride ligands (Os)H_t without participation of the terminal hydrogen atoms (B)H_t proceeds *via* a transition state in which the metal is coordinated to the B–H bond.¹⁰

The data presented above demonstrate that the existing view about the exceptionally high fluxionality of transition metal tetrahydroborate complexes needs to be corrected. Individual signals for the terminal and bridging protons cannot be observed (with only one exception⁶⁵) only for compounds of Group I, III and IV transition metals. Among Group V–VIII transition metal compounds, many complexes do give rise to separate NMR signals for the terminal and bridging protons of the BH_4 ligands. The fluxionality decreases with an increase in the size of the

stabilising ligands. This has been shown in relation to the iron complex $\text{FeH}(\text{BH}_4)_2$ ($\text{L} = \text{DMPE}$, DEPE , DPrPE) and a niobium complex with the Cp and Cp^* ligands, respectively.^{123, 169} The results of analysis of the activation energy for the exchange of bridging and terminal protons suggest that the fluxionality of the complexes decreases also on passing from Group V metals to Group VIII metals and from $3d$ metals to $4d$ or $5d$ metals (see Table 2). Thus, the decrease in the fluxionality of tetrahydroborates occurs in the same direction as the decrease in their thermal stability mentioned above. The correlation observed between these properties might be due to the fact that a decrease in the fluxionality is indicative of an increase in the degree of covalency of the $\text{M}-\text{H}_b$ bond, which increases the probability of decomposition of tetrahydroborate complexes by the oxidative addition mechanism ($\text{MBH}_4 \rightarrow \text{HMBH}_3$).

IV. Possible reasons for the differences in the structural and dynamic properties of tetrahydroborate complexes

What is the reason for the so sharp differences in the types of ligand coordination and in the structural and dynamic properties of the complexes formed by Group III and IV transition metals and those formed by Group I, V–VIII transition metals? The attempts to rationalise the structure of tetrahydroborate complexes in terms of the Coulomb interaction between the BH_4^- anions and metal cations (with the assumption that enhancement of the Coulomb forces should increase the degree of covalence of the metal–boron bond and the denticity of the BH_4 ligand²²⁷) do not provide satisfactory results. The attractive force between the anion and the central atom in many complexes of Group I, V–VIII transition metals should be greater than that in Group III and IV metal complexes because the ratio of the ion charge to the ionic radius squared (z/r^2) for, for example, $\text{Fe}(\text{II})$, $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ is greater than this ratio for $\text{U}(\text{III})$ or cerium subgroup lanthanides. Nevertheless, the denticity of the BH_4 ligand is lower in the former type of complexes.

Since the oxidation number of the central atoms in most of the Group I, V–VIII transition metal tetrahydroborates is +2, while that in the complexes of Group III and IV transition metals is +3 or +4, one can suggest that the difference in the ligand denticity is related to the oxidation state of the central atom. However, this suggestion is at variance with the existence of a number of bidentate complexes of Group V–VIII transition metals containing the central atom in the +3 and +4 oxidation state [for example, $\text{Ir}(\eta^2\text{-BH}_4)_2\text{H}_2(\text{PBu}_3)_2$, $\text{WH}_3(\eta^2\text{-BH}_4)(\text{PMe}_3)_3$, $\text{OsH}_3(\eta^2\text{-BH}_4)(\text{PPr}_3)_2$]; conversely, complexes of divalent ytterbium contain tetrahydroborate groups coordinated in the tridentate manner (see Table 1).

The most widespread hypothesis states that the tetrahydroborate ligand in the complexes is linked to the central atom *via* covalent two-electron three-centre $\text{M}-\text{H}-\text{B}$ bonds and is isolobal to the chloride, allyl or cyclopentadienyl anion, *i.e.* it acts as a two-, four- or six-electron donor, depending on the denticity. According to this hypothesis, the type of coordination (η^n) of the BH_4 ligand corresponds to the number n of electron pairs provided by this ligand and the ligand denticity is determined by the tendency of the central atom to fill the outer electron shell and can be predicted using the effective atomic number (EAN) rule.^{228–230}

However, the attempts to apply this approach to a broad range of objects showed that predictions based on this hypothesis often do not comply with experimental data regarding both chemical and physical properties of tetrahydroborate complexes, or with the EAN rule. For example, in conformity with this hypothesis, $\text{Cu}(\eta^2\text{-BH}_4)(\text{phen})(\text{PPh}_3)$ and $\text{Cp}_2\text{M}(\eta^2\text{-BH}_4)_2$ ($\text{M} = \text{Zr}$, Hf) should be 20-electron complexes, $\text{Y}(\eta^2\text{-BH}_4)(\eta^3\text{-BH}_4)_2(\text{THF})_3$ should be 22-electron, $\text{M}(\eta^3\text{-BH}_4)_4$ ($\text{M} = \text{Zr}$, Hf) should be 24-electron, and $[\text{Zn}(\eta^2\text{-BH}_4)_4]^{2-}$ should even be a 26-

electron complex.²³¹ This hypothesis cannot also interpret the change in the type of coordination in the pairs of isoelectronic complexes $\text{Sc}(\eta^2\text{-BH}_4)(\eta^3\text{-BH}_4)_2(\text{THF})_2$, $\text{Y}(\eta^3\text{-BH}_4)_3(\text{THF})_2$ and $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Pr}(\eta^3\text{-BH}_4)$, $(\text{MeOCH}_2\text{CH}_2\text{C}_5\text{H}_4)_2\text{Yb}(\eta^2\text{-BH}_4)$. The paramagnetism of the vanadium $\text{V}(\eta^2\text{-BH}_4)_3(\text{PMe}_3)_2$ ($\mu_{\text{eff}} = 2.5 \mu_{\text{B}}$),⁸⁴ chromium $(\text{TMEDA})\text{Cr}(\eta^2\text{-BH}_4)_2$ ($\mu_{\text{eff}} = 4.8 \mu_{\text{B}}$),⁹³ and cobalt $\text{Co}(\eta^2\text{-BH}_4)[\text{MeC}(\text{CH}_2\text{PPh}_2)_3]$ ($\mu_{\text{eff}} = 3.1 \mu_{\text{B}}$)¹⁰⁹ complexes considered in terms of this hypothesis does not agree with the denticity of the BH_4 ligands found for these complexes. The Lewis acidity of the allegedly 18-electron complex $\text{Zn}(\eta^2\text{-BH}_4)_2$ (see Ref. 231) and the 24-electron complexes $\text{M}(\eta^3\text{-BH}_4)_4$ ($\text{M} = \text{Zr}$, Hf) cannot be explained either.^{232, 233} When the number of electrons is calculated in this way, deviations from the EAN rule are observed for many structurally characterised transition metal tetrahydroborates; the deviation increases with an increase in the number and denticity of the BH_4 ligands in the complex, which indicates that this method overestimates the number of electrons donated by the tetrahydroborate ligand.

It should also be noted that, in accordance with the views considered above,^{222–230} the strength of the metal–tetrahydroborate ligand bond should increase with an increase in the number of $\text{M}-\text{H}$ ‘covalent’ bonds, *i.e.* with an increase in the ligand denticity. This, in turn, should result in an increase in the stereochemical rigidity of complexes on passing from monodentate to bi- and then to tri-dentate coordination of BH_4 groups. However, experimental results point to an opposite trend, namely, complexes with η^2 - and even η^1 - BH_4 groups are stereochemically more rigid than complexes with η^3 - BH_4 ligands.

Thus, the hypothesis that, depending on its denticity, the BH_4 group is isolobal to chloro, allyl or cyclopentadienyl ligand cannot explain and predict correctly the chemical, physical or structural properties of transition metal tetrahydroborates. Data on a decrease in the fluxionality of complexes with η^3 - BH_4 groups with respect to the complexes with η^2 - BH_4 and η^1 - BH_4 groups point to a low contribution of covalent interaction to the bond of the metal with the BH_4^- anions, at least, for Group III and IV transition metals. This conclusion is in agreement with the results of calculations carried out for the $\text{L}_{4-n}\text{Cu}-\text{H}_n-\text{BH}_{4-n}$ complexes ($n = 1, 2, 3$), which showed a largely ionic character of the $\text{Cu}-\text{H}_n-\text{BH}_{4-n}$ bond and electrostatic nature of the interaction between the coordinated copper atom and the BH_4^- anion with a relatively small contribution of the covalent bond.²³⁴ This conclusion is also consistent with the results of a study of copper tetrahydroborate complexes by mass spectrometry with extraction of ions from the solution (electro-spray mass spectrometry).^{235, 236}

The change in the type of coordination of the BH_4 ligands in Group III and IV transition metal complexes is much better explained by the influence of purely steric properties of ligands if one assumes that these complexes tend to fill the coordination sphere of the central atom as fully as possible and that a tridentate coordination of the BH_4 group to the metal atom, which implies the largest volume occupied by this group, is the most favourable. It is assumed that this type of coordination is always realised whenever it is allowed by the spatial conditions in the complex and that transition to other types of coordination is induced by the influence of steric factors. On this basis, a procedure for the calculation of the degree of occupancy of the metal coordination space was developed and convincing examples confirming the efficiency and predictive capacity of this approach were cited.^{237 †} The trend to fill the coordination sphere of the central atom as fully as possible and the high coordination numbers typical of tetrahydroborates of Group III and IV transition metals attest to a high degree of ionicity of the $\text{M}-\text{BH}_4$ bond, which is consistent with the substantial fluxionality of these compounds.

Nevertheless, several examples demonstrate that the scope of this approach is also limited. It is mainly applicable to Group III

† Unfortunately, only few steric constants of ligands are given in the study cited,²³⁷ which narrows down the scope of application of this method.

and IV transition metal compounds, although with exceptions. For example, only half of the BH_4 groups in the $[\text{La}(\eta^3\text{-BH}_4)_2(\eta^2\text{-BH}_4)_2(\text{THF})_2]^-$ anion are coordinated as η^3 -ligands, despite the fact that the metal coordination sphere is filled only to 86%.¹⁸ This approach cannot be used to interpret the structure of complexes formed by transition metals of other groups. For example, in the $[\text{Mn}(\eta^2\text{-BH}_4)_3(\text{THF})]^-$ and $[\text{Zn}(\eta^2\text{-BH}_4)_3]^-$ anions, the BH_4 ligands have η^2 -coordination,^{100, 101, 134} although the coordination spheres of the central atom are filled only to 86% and 75%, respectively.

Thus, in the general case, the difference between the types of coordination of the BH_4 ligands in transition metal compounds cannot be explained by either the influence of the oxidation state of the central atom, or the different electrostatic interaction of the metal with the ligands, or by the 'tendency' of the central atom to fill the outer electron shell, or by the influence of spatial factors.

Analysis of the data presented in Tables 1, 2 suggests that the main factor determining the differences between the structures and dynamics of the tetrahydroborate complexes of Group III and IV transition metals, on the one hand, and Group I, V–VIII metals, on the other hand, is the difference between the electronic configurations of the central atoms.

The electronic configuration of Group III and IV transition metals in compounds with tridentate tetrahydroborate ligands (except for the complex of zerovalent titanium with carbonyl groups⁶⁵) is d^0 (or d^1 in the case of complexes of trivalent titanium). In the complexes of Group I, V–VIII transition metals, the central atom with the d^n -configuration ($n = 2–10$) has at least two electrons not involved in the formation of the chemical bonds in the outer d shell. The fact that no examples of structurally characterised complexes of these metals with tridentate BH_4 ligands are available suggests that the presence of two or more electrons in the outer d shell destabilises the η^3 -coordination and, therefore, the η^2 -coordination becomes more favourable from the energy standpoint. Thus, whereas the bidentate coordination is sterically forced in complexes with central atoms having the d^0 - and d^1 -configuration, in the case of ions with d^n -configurations ($n = 2–10$), it is the η^2 -coordination that is realised without steric restrictions.

The increase in the stereochemical rigidity of complexes on passing to compounds of Group V–VIII metals can be accounted for by the presence of electrons in the outer d shell which do not participate in the formation of chemical bonds and decrease the energetic profitability of the most probable rearrangement pathway $\eta^2-\eta^3-\eta^{2'}$.⁵⁷ Indeed, quantum-chemical calculations¹⁰ showed that $\eta^2-\eta^1-\eta^{2'}$ is an energetically more favourable pathway for the exchange of the bridging and terminal protons of the BH_4 group in the complex $\text{Os}(\eta^2\text{-BH}_4)_3(\text{PPt}_3)_2$.

In conformity with the above-noted crucial influence of the electronic configuration of the central atom on the structural and dynamic properties of the tetrahydroborate ligands in the complex, derivatives of titanium group metals with the oxidation number +2 should contain bidentate BH_4 ligands. In fact, no examples of Ti(II) compounds with tridentate BH_4 groups are available; in the d^2 -complexes, $\text{Cp}^*\text{Ti}(\eta^2\text{-BH}_4)[(\text{Me}_2\text{PCH}_2)_3\text{SiBu}^t]$ and $\text{Ti}(\eta^2\text{-BH}_4)_2(\text{DMPE})_2$, the BH_4 groups are coordinated as bidentate ligands.^{54, 55} However, in the d^0 -complex $\text{Yb}(\eta^3\text{-BH}_4)_2(\text{Py})_4$, these ligands are tridentate,²² despite the substantially greater ionic radius of the central atom, which decreases the Coulomb interaction.

In this connection, we would like to mention the well-known influence of lone electron pairs on the structure of coordination compounds explained by repulsion of the coordinated ligands from non-bonding electrons.²³⁸ It was noted that, when the number of non-bonding d electrons is 1 to 3, their effect on the structural properties of molecules is normally too low to be detected experimentally. However, the examples considered above demonstrate that the type of coordination and the dynamic behaviour of the BH_4 ligand change crucially even in the presence of two non-bonding outer d electrons.

As any other corollary based on the generalisation of experimental data, this assumption leaves room for exceptions the discovery and analysis of which would result in further development of the views on the structures of the compounds considered. To verify the assumption concerning the reasons for the differences in the modes of coordination and dynamic properties of BH_4 ligands, it is necessary, in particular, to study complexes of Group IV transition metals with the central atom in a low oxidation state and to develop methods for the synthesis and study of compounds of Group V–VIII metals in high oxidation states.

V. Complexes of post-transition metals with terminal BH_4 ligands

The assumption that metal d electrons destabilise the η^3 -coordination of the BH_4 groups more significantly than the η^2 -coordination relied on analysis of the results of quantum-chemical calculations for complexes with central d^{10} ions.^{239, 240} It was suggested that this destabilisation should decrease the difference between the energies of η^2 - and η^3 -coordinated groups and thus enhance the fluxionality of tetrahydroborate complexes. Indeed, no data about non-equivalence of the terminal and bridging protons in the tetrahydroborate complexes with d^{10} -configuration of the central atom can be found in the literature. Moreover, experimental data point to specific properties of the complexes in which the outer d shell of the metal ions is either half or completely filled (d^5 or d^{10}). Thus Mn(II) , Cu(I) and Zn(II) complexes are much more numerous and thermally stable than complexes of other Group V–VIII transition metals or post-transition metals.

It could be suggested that the presence of a filled d shell influences not only the thermal stability of the complex but also the mode of coordination of the BH_4 groups. However, it can be seen that both post-transition metals (Zn , Cd , Hg , Ga , In) having a closed outer d^{10} shell and Group I and V–VIII transition metals having d^n -configurations ($n = 2–10$) tend to be coordinated by BH_4 in a bidentate fashion even in those cases where steric factors are favourable for η^3 -coordination (see Table 1). Indeed, the complexes $\text{Zn}(\eta^2\text{-BH}_4)_2$ and $[\text{Zn}(\eta^2\text{-BH}_4)_3]^-$ contain bidentate BH_4 ligands, despite the fact that the metal coordination sphere is not 100% full {in $[\text{Zn}(\eta^2\text{-BH}_4)_3]^-$, it is only 75% full}. Apparently, even a closed outer d -shell destabilises η^3 -coordination, although, due to its higher symmetry, a less pronounced destabilisation of the complex should be expected in this case.

The paucity of post-transition metal complexes the structures of which are known can be explained by their low thermal stability (see Table 1). The complex $\text{Cp}(\text{CO})_2\text{FeGa}(\eta^2\text{-BH}_4)[(\text{CH}_2)_3\text{NMe}_2]$ is the only example, among gallium tetrahydroborate complexes with terminal BH_4 groups, the structure of which has been established by X-ray diffraction analysis.¹⁴³ The structural data for other gallium complexes presented in Table 1 have been obtained by gas phase electron diffraction analysis. No examples of structurally characterised tetrahydroborate complexes of mercury, indium or thallium can be found in the literature. However, the conclusion about bidentate coordination of the BH_4 ligand in $\text{Me}_2\text{In}(\eta^2\text{-BH}_4)$ has been drawn on the basis of IR-spectroscopic data.¹⁴⁴ The IR spectra of the tetrahydroborate complexes of post-transition metals reported in the literature generally comply, in the region of stretching B–H vibrations, with those expected for bidentate BH_4 groups (see Table 1).

The synthesis of tetravalent germanium and tin tetrahydroborates $\text{M}(\eta^3\text{-BH}_4)_4$ ($\text{M} = \text{Ge}$, Sn) has been reported;²⁴¹ they were obtained as solid compounds stable in air up to 473 K and containing tridentate (according to IR spectroscopy) tetrahydroborate ligands. An estimate of the degree of filling of the coordination sphere in these compounds, which we performed using published data,^{223, 237} showed that in the case of Ge(IV) , η^3 -coordination of the four BH_4 groups is unlikely because the coordination sphere of the central atom is overcrowded, while the Sn(IV) coordination sphere in $\text{Sn}(\eta^3\text{-BH}_4)_4$ should be filled to 100%. Covalent tetrahydroborates with filled coordination

spheres of the metal atoms should be volatile compounds unstable in air, like $\text{Zr}(\eta^3\text{-BH}_4)_4$. Therefore, the properties described for tetravalent germanium and tin tetrahydroborates, and even the mere fact of existence of these compounds, appear doubtful. It is noteworthy that reports concerning the syntheses of unusual tetrahydroborate complexes of transition metals, such as Cp_3CeBH_4 ²⁴² and $\text{Cp}_2\text{MO}(\eta^2\text{-BH}_4)_2$ ($\text{M} = \text{Mo}, \text{W}$),²⁴³ have been published and repeatedly cited, although subsequent attempts to reproduce them failed.^{244, 245}

VI. Complexes of Group IA and IIA metals and aluminium with terminal BH_4 ligands

The structures of alkali and alkaline earth tetrahydroborate complexes are little studied. Among alkali metal complexes, lithium compounds have been studied most comprehensively. Table 1 presents several examples of complexes of univalent lithium with η^2 - and η^3 -coordinated BH_4 ligands. Antsyshkina *et al.*¹⁴⁶ believe that the complex $\text{LiBH}_4(18\text{C}6)$ in the crystalline state contains a η^1 -coordinated BH_4 group. The same structure was proposed¹⁴⁶ for $\text{NaBH}_4(15\text{C}5)$.¹⁵⁰ However, the conclusions about the monodentate coordination of the tetrahydroborate ligands are inconsistent with the experimental data on the $\text{M}\cdots\text{B}$ distances in these complexes, which are close to the value expected for $\eta^2\text{-BH}_4$.²²³ Despite the fact that no data on the structures of tetrahydroborates of heavier metals ($\text{K}, \text{Rb}, \text{Cs}$) are available to date, it can be suggested that these metals, like lithium, form compounds with all the main types of coordination of BH_4 . The difference between the structures of $\text{Li}(\eta^3\text{-BH}_4)[\text{HC}(3,5\text{-Me}_2\text{pz})_3]$ and $\text{Cd}(\eta^2\text{-BH}_4)[\text{HB}(3,5\text{-Me}_2\text{pz})_3]$, noted by Reger *et al.*,¹⁴⁵ namely, the fact that the BH_4 group is coordinated in the bidentate fashion to the $\text{Cd}(\text{II})$ ion having a greater size and a higher charge, whereas it is coordinated as a tridentate ligand to the $\text{Li}(\text{I})$ ion, can be understood in view of the assumption about destabilising influence of outer d electrons.

The similarity of the structural and spectral properties of TiBH_4 to those of alkali metal tetrahydroborates^{1, 2} is also consistent with this assumption because the closed $5d^{10}$ shell of the $\text{Ti}(\text{I})$ ion is shielded by the filled $6s^2$ shell, which diminishes the destabilising influence.

The type of BH_4 coordination in $\text{CpBe}(\eta^2\text{-BH}_4)$ could not be established unambiguously from electron diffraction data. The conclusion about the bidentate coordination of this ligand to the beryllium atom was drawn resorting to the data of IR spectroscopy.^{151, 152} The denticity of BH_4 ligands in alkaline earth metal complexes ($\text{Ca}, \text{Sr}, \text{Ba}$) corresponds to that expected on the basis of steric considerations — BH_4 groups accomplish tridentate coordination whenever the spatial possibility exists. No structural data pointing to the possibility of η^3 -coordination of BH_4 groups in magnesium or aluminium complexes are currently available. In this connection, recall that the ionic radii of $\text{Al}(\text{III})$ and, especially, $\text{Be}(\text{II})$ are much smaller than those of transition metals.²²²

The type of coordination of tetrahydroborate ligands in the metal complexes in question cannot be determined from the data of NMR spectroscopy; these data attest to equivalence of all the four protons in the BH_4 ligand.^{145, 147, 148, 157, 161} The data of IR spectroscopy for alkali and alkaline earth metal complexes do not conform to any particular type of coordination of the tetrahydroborate groups either.^{145, 147, 148, 157}

The structures of the tetrahydroborate complexes with the central d^0 -metal ions in the oxidation state +1 as well as complexes with the d^n -metal central ions ($n = 2-10$) cannot be explained in terms of the principle of the maximum occupancy of the coordination sphere. Calculations using this principle²³⁷ provide the best results in the case of complexes with $d^0(d^1)$ -metal central ions in the oxidation states +3 or +4 and with ionic radii ranging from 0.7 to $\sim 1 \text{ \AA}$. Calculations performed in conformity with the data reported by Edelstein²²³ show that tridentate coordination of BH_4 groups in tetrahydroborates of metals with ionic radii of less than 0.68 $\text{\AA}$ (the difference between

the radii of the ionic and tridentate forms of BH_4) requires that the metal—boron distances be smaller than the radius of the BH_4^- anion. Therefore, the deviations from the principle of the maximum occupancy of the coordination sphere observed for these ions can be attributed to the mutual repulsion of ligands. For d^0 -metal ions in the oxidation state +2, this principle can be used to estimate the probable denticity of the BH_4 ligands; however, the maximum occupancy of the metal coordination sphere is seldom encountered. Apparently, under normal conditions, the number of neutral ligands (for example, ethers) these ions can hold is insufficient to fill completely their coordination sphere. Thus, the scope of application of the principle of the maximum occupancy of the coordination sphere of the central atom for predicting the structures of tetrahydroborate complexes is mainly limited to complexes with central d^0 -metal ions in the oxidation states +3 and +4.

VII. Tetrahydroborate complexes with bridging BH_4 ligands

The structurally characterised compounds with bridging tetrahydroborate groups are presented in Table 3. Comparison of the data of Tables 1 and 3 shows that alkali metal complexes with bridging BH_4 ligands are as prevalent as complexes with terminal tetrahydroborate ligands. On passing to alkali earth metals, lanthanides and actinides, the proportion of compounds with bridging BH_4 groups in the whole set of structurally characterised compounds gradually decreases; no structurally characterised bi- or polynuclear complexes of Group IV and V transition metals with tetrahydroborate bridges between the metal atoms are known. The trend to form complexes with bridging BH_4 groups then starts increasing again and, for Group VIII metals, the fractions of complexes with known structures containing terminal and bridging BH_4 groups are nearly equal. These data suggest that the formation of bridged compounds is facilitated by a decrease in the charge and an increase in the radius of the complex-forming ion.

The most frequently encountered polynuclear complexes (14 of 39, see Table 3) are those in which two metal atoms are bound in the η^2 -fashion to the opposite edges of a BH_4 tetrahedron (see Fig. 2a). None of the tetrahedron vertices belong simultaneously to both metal atoms. Each hydrogen forms μ_2 -bridges between boron and the metal, *i.e.* the BH_4 groups are generally tetradentate. Depending on the oxidation state of the metal, the number of BH_4 tetrahedra, the nature of the stabilising ligands and crystallisation conditions, this type of coordination of bridging groups results in the formation of dimers,^{189, 212, 213, 216} infinite polymer chains,^{160, 200, 202, 217} a two-dimensional network,²¹⁰ or a three-dimensional network.^{147, 207, 208} Apparently, three-dimensional structures of this type are also formed in some non-solvated compounds $\text{M}^n(\text{BH}_4)_n$ ('ionic' tetrahydroborates).

In a less abundant (six complexes) type of coordination, the BH_4 group is bound by two edges to two metal atoms and the edges participating in the coordination share a vertex ($\mu_3\text{-H}$). One hydrogen remains free from binding to the metal atoms; thus, the BH_4 groups are in total tridentate (see Fig. 2b). This pattern of coordination results most often in the formation of dimeric complexes^{145, 148, 198, 214} and in some cases, polymer chains.¹⁹⁹

There is only one compound ($\text{LiBH}_4 \cdot \text{Et}_2\text{O}$) in which the BH_4 group is coordinated to three metal atoms (to each of them, by an edge); these three edges share a vertex ($\mu_4\text{-H}$, see Fig. 2c).^{147, 197} In the crystals of $\text{LiBH}_4(\text{MeOBU})$, the BH_4 group is also coordinated by its edges to three metal atoms; however, there is no vertex common to these three edges (see Fig. 2d). In these cases (see Fig. 2c,d), all the four hydrogen atoms are involved in the formation of bridging bonds, *i.e.* the BH_4 group is tetradentate.

The η^1, η^2 -bridging coordination is represented by two examples, $\text{Mn}_2(\text{CO})_5(\text{DPPM})\text{H}(\text{BH}_4)$ and $\text{GaH}_2(\text{BH}_4)$; in this case, one metal atom is coordinated to an edge of the tetrahedron, while the other one is bound to the opposing vertex (see Fig. 2e).^{174, 221} The

η^1, η^1 -coordination according to which each of the two metal atoms is bound to one tetrahedron vertex (see Fig. 2f) is represented by six examples.^{93, 173, 178, 196, 221} This gives rise to a chain or a ring with the $M-H-BH_2-H-M$ sequence of bonds; two hydrogen atoms remain in the terminal positions.

The complex $GaH_2(BH_4)$ in the crystalline state forms a polymer chain consisting of alternating BH_4 tetrahedra with the types of coordination shown in Fig. 2e,f, so that the coordination numbers of the gallium ions are 4 and 6.²²¹

There exists one example, $HFe_3(CO)_9(BH_4)$, of η^1, η^1, η^1 -coordination of the BH_4 ligand where three metal atoms of the cluster are bound to three vertices of the BH_4 tetrahedron (three μ_2 -H bonds; the overall denticity of the tetrahydroborate ligand is η^3 , see Fig. 2g).¹⁷⁷ Conversely, in the Na_4B_4 heterocubane core of the $[NaBH_4(TMTCN)]_4$ tetramer, each three neighbouring sodium atoms are linked to the same vertex of the BH_4 tetrahedron (μ_4 -H bond; the total denticity of the BH_4 group is η^1 , Fig. 2h).¹⁴⁸

Among mercury complexes, two compounds, $[cyclo-(o-C_6F_4Hg)_3] \cdot (BH_4)_2(Bu_4N)_2$ and $[cyclo-(o-C_6F_4Hg)_3]_2(BH_4) \cdot (Bu_4N)$, have been isolated in an individual state.²¹⁹ Their structures have not been determined. Relying on the results of quantum-chemical calculations, it was assumed that the BH_4 ligand in $[cyclo-(o-C_6F_4Hg)_3] \cdot (BH_4)(Bu_4N)$ is linked to one mercury macrocycle as shown in Fig. 2g and to one more macrocycle as shown in Fig. 2h,²²⁰ i.e. this group is supposed to be connected simultaneously to six metal atoms.

A type of coordination in polynuclear complexes represented rather widely (six structures) is the coordination according to which one or two metal atoms are bound to a face of the BH_4 tetrahedron, which corresponds to η^3 -coordination in mononuclear complexes (see Fig. 2i, total denticity η^4 , and Fig. 2j, total denticity η^3). However, as in the case of mononuclear complexes, this coordination pattern is encountered only for metal ions having no outer *d* electrons, i.e. sodium,¹⁴⁸ strontium(II), barium(II),¹⁵⁷ cerium(III),²⁰³ samarium(III),²⁰⁴ and neodymium(III),²⁰⁵ whereas no examples of face coordination (η^3) are known for *dⁿ* ions ($n = 2-10$) (see Table 3).

In the NMR spectra of complexes of Group I, II, III and IV metals with BH_4 bridges, separate signals for the terminal and bridging protons have not been detected. The non-equivalence of protons of the bridging BH_4^- ligands has been observed in the NMR spectra of complexes of Group VII–VIII transition metals.^{173, 174, 177, 178, 188, 196} Thus, the structure and the dynamic behaviour of polynuclear compounds with BH_4 bridging groups also does not contradict the assumptions made in this study.

The data presented in Table 3 demonstrate a fundamental difference between the complexes with central *d⁰*-metal ions and the complexes with *dⁿ* transition metal ions ($n = 2-10$), namely, in the case of alkali and alkaline earth metals, lanthanides and uranium, the tetrahydroborate bridges connect neutral mononuclear molecular units, which results in a fuller occupancy of the metal coordination sphere and corresponds to the non-directionality and non-saturability of the mainly ionic $M-BH_4$ bond in these compounds. In the case of Group I and V–VIII transition metals, the tetrahydroborate bridges are formed between cationic species or, in most cases, between metal atoms bound into a cluster and located close to each other. The example of the cobalt complex $[Co(DPPP)(BH_4)]_2$ seemingly contradicts this conclusion. However, the low magnetic moment of this complex points to the presence of a metal–metal bond.²¹⁴ Hence, in this case, too, the formation of the tetrahydroborate bridges is favoured by the presence of a bond between transition metal atoms. Among post-transition metal complexes, there are compounds with polymer chains consisting of neutral molecules connected *via* tetrahydroborate bridges, for example, $[MeZnBH_4]_\infty$ ^{217, 218} and $[GaH_2(BH_4)]_\infty$.²²¹

The fluxionality, η^3 -coordination and the trend for the maximum occupancy of the coordination sphere are as typical of lanthanide and actinide complexes as of complexes formed by *d* metals with *d⁰* central ions. Therefore, it can be concluded that *f*

electrons do not influence the properties of tetrahydroborate complexes as substantially as outer *d* electrons. It has been suggested^{5, 207} that *f* orbitals participate in the formation of the bonds of the central atom with the BH_4 groups. However, in our opinion, the available data do not provide grounds for this suggestion.

In the structures which have now been determined, one to three metal ions are connected to one BH_4 group *via* its vertices or edges, or one or two metal ions are coordinated to this BH_4 group *via* faces. The metal ions in one structure can be coordinated both in the same way and in different ways; however, not all the possible combinations of various types of coordination have been confirmed experimentally. Thus a complex in which three metal ions are bound to the same vertex of the BH_4 tetrahedron in the monodentate fashion is known but there are no examples of complexes in which two or more metal ions are coordinated in the bidentate fashion to the same edge or in the tridentate fashion to the same face of the tetrahedron. Examples of structurally characterised complexes in which four or more metal ions are linked to one BH_4 group or examples of heteronuclear complexes in which this group serves as a bridge between ions of different metals cannot be given either. In the majority of polynuclear complexes ($\sim 60\%$ of the total number), all the four hydrogen atoms of the BH_4 groups are involved in coordination, i.e. they are formally tetradentate ligands (see Fig. 2a,c,d,f). About one-fourth of the complexes studied (see Fig. 2b,e,g) contain BH_4 ligands with one non-coordinated hydrogen atom. There are only a few polynuclear complexes with tetrahydroborate bridges formed by one (see Fig. 2h) or two (see Fig. 2f) hydrogen atoms.

Unlike compounds with terminal tetrahydroborate ligands, for bridging complexes, no correlation has been found between the data of IR spectroscopy and the types of coordination of bridging groups.

It has been noted¹⁹⁸ that the hypothesis of three-centre two-electron type of the $M-H-B$ bond is inapplicable for calculation of the EAN in the compounds with bridging BH_4 groups.

VIII. Conclusion

Analysis of experimental data on the structure of tetrahydroborate complexes makes it possible to elucidate a series of correlations between the structural or dynamic properties of these compounds and the nature of the central atom and stabilising ligands.

Compounds of Group III and IV transition metals (lanthanides, U, Ti, Zr, Hf) have been studied most comprehensively. In addition to the diversity of stabilising ligands, these complexes are characterised by diverse modes of coordination of tetrahydroborate ligands (η^1 -, η^2 - and η^3 - BH_4 , various types of BH_4 bridges between neutral species); complexes with BH_4 ligands of different denticities at one metal atom are also known. Most of complexes containing these metals in the oxidation states +3 and +4 comply with the principle of the maximum occupancy of the metal coordination sphere. The known tetrahydroborates of these metals possess clear-cut fluxionality (the protons of the BH_4 group are equivalent on the NMR time scale). Only for the complex $[Ti(CO)_4(\eta^3-BH_4)]-[K(18C6)]^+$, were the signals of the terminal and bridging protons of η^3 - BH_4 distinguished in low-temperature NMR spectra.

The structures of alkali and alkaline earth metal tetrahydroborates have not been adequately studied. As indicated by the available data, characteristic features of these compounds include fluxionality, diversity of the modes of coordinations of tetrahydroborate ligands to metals, formation of BH_4 bridges between neutral molecular units; the principle of the maximum occupancy of the coordination sphere is often violated.

The structural chemistry of Group I and V–VIII transition metal tetrahydroborates is much less plentiful than that for the Group III and IV transition metals; the range of stabilising ligands is more limited; no complexes with η^3 - BH_4 groups or with BH_4

bridges between neutral molecular units have been found. The principle of the maximum occupancy of the coordination sphere is not obeyed for these compounds.

In the complexes of Group I and V–VIII transition metals, BH_4 groups tend to be coordinated as mono- and bidentate ligands. Monodentate coordination is found only when the coordination sphere contains bulky ligands having strong electron-donating properties (phosphines, macrocyclic compounds), *i.e.* it is a forced type of coordination. The factors inducing the formation of complexes of these metals with mono- and bidentate coordination of the BH_4 ligands are not entirely clear yet. Whereas alkali, alkaline earth and rare earth metals and uranium tend to form polynuclear complexes due to tetrahydroborate bridges between neutral mononuclear molecules, in the case of Group I and V–VIII metals, the BH_4 bridges connect either cationic species or metal atoms bound into a cluster and located close to one another.

Tetrahydroborates of Group V–VIII transition metals possess higher stereochemical rigidities than complexes of Group IA, IIA, IIIB and IVB metals. For many of them, separate signals for terminal and bridging protons of mono- and bidentate BH_4 groups can be detected in low-temperature NMR spectra. In some of the compounds considered, the exchange of terminal and bridging protons does not proceed at a noticeable rate even at room or higher temperature. In some cases, bridging protons give rise to two separate NMR signals and the exchange of non-equivalent bridging protons with terminal protons occurs at different rates.

The absence of a trend for the maximum occupancy of the coordination sphere, the low coordination numbers and an increase in the stereochemical rigidity indicate that the degree of covalence of the $\text{M}-\text{BH}_4$ bond in Group V–VIII metal tetrahydroborates is higher than that in the Group IA, IIA, IIIB and IVB metal complexes.

Neither resorting to the views on the three-centre two-electron $\text{M}-\text{H}-\text{B}$ bond, widely employed now, nor allowing for steric factors can substantiate in the general case the observed structures and some physical and chemical properties of tetrahydroborate complexes.

Analysis of the experimental data presented above led to the assumption that the crucial factor determining the differences in the structures and the dynamic properties of transition metal tetrahydroborate complexes is the electron configuration of their central ions, which is d^0 (d^1) for most of the Group III and IV metal compounds considered or d^n ($n = 2-10$) for Group I and V–VIII metal complexes. High coordination numbers, the trend for the maximum occupancy of the coordination sphere and fluxionality of the tetrahydroborates of Group IA, IIA, IIIB and IVB metals indicate that the $\text{M}-\text{BH}_4$ bonds in these compounds are mostly ionic. The fluxional behaviour of these compounds is apparently related to the fact that the spherically symmetrical electron shell of d^0 ions does not create barriers to free rotation of the BH_4^- anion in the metal coordination sphere. In the complexes with central d^n ions ($n = 2-8$), the mutual repulsion of the non-bonding d -electrons and coordinated BH_4^- anions destabilises the η^3 -coordination of the BH_4 groups, which makes the most probable rearrangement pathway ($\eta^2-\eta^3-\eta^2$) energetically less favourable and results in an increase of the stereochemical rigidity of complexes of Group V–VIII metals. In addition, this factor prevents the formation of tetrahydroborate bridges between neutral mononuclear molecules in d^n -metal tetrahydroborates ($n = 2-8$). Complexes with central d^{10} ions, possessing completely filled d -electron shells, occupy an intermediate position — there are no complexes with η^3 -groups among them but stereochemically rigid complexes have not been found either.

The similarity of the structural and dynamic properties of tetrahydroborate complexes formed by f elements and those with central d^0 ions (η^3 -coordination, fluxional behaviour and the trend for maximum occupancy of the metal coordination sphere) leads to the conclusion that f electrons do not influence the properties of

tetrahydroborate complexes as significantly as outer d electrons and they apparently do not participate in the formation of bonds of the central atom with the BH_4 ligand.

The data considered above provide information not only on the dependence of the structural and dynamic properties of the tetrahydroborate ligand on the electronic configuration of the central atom but also on the dependence of the coordination and, correspondingly, catalytic properties of the central atom on the structure of its outer electron shell.

Since the tetrahydroborate anion is isoelectronic with the methane molecule, tetrahydroborates can be regarded as models of some steps of $\text{C}-\text{H}$ bond activation in saturated hydrocarbons.³ It is noteworthy in this connection that the sharp difference between the coordination (and, hence, catalytic) properties of the complexes with central d^0 and d^n ions ($n = 2-10$) is also manifested in many systems related to the transformations of hydrocarbon ligands. Thus activation of methane and cyclo-metallation reactions with participation of d^0 -ion complexes follow a mechanism which includes a multicentre transition state,²⁴⁶ whereas activation of $\text{C}-\text{H}$ bonds involving complexes with central d^n ions often proceeds according to an oxidative addition mechanism, similar to the exchange of hydride ligands and bridging hydrogen atoms in $\text{OsH}_3(\text{BH}_4)(\text{PPr}_3)_2$.¹⁰

It is also known that transition metal metallocene complexes with central d^0 ions act, under certain conditions, as active catalysts for polymerisation of α -olefins according to the so-called metallocene catalysis mechanism.²⁴⁷ Similar complexes with d^n ions do not exhibit pronounced catalytic activity under the same conditions; the catalysts of α -olefin polymerisation based on d^n ions have a different composition, 'work' under different conditions and by a different mechanism.²⁴⁸ By analogy with the BH_4 ligand, hydrocarbon ligands might possess different stereochemical rigidities and different denticities in the coordination with d^0 or d^n ions.

Further studies of structural and dynamic properties of the tetrahydroborate complexes with central d^0 and d^n ions are needed to understand the nature of the metal–ligand bond in these complexes. They are also required for development of the general views on the fluxional behaviour, for more extensive investigations of the dependence of the coordination and catalytic properties of metals on the electronic structures of their atoms and for modelling of the transition states in hydrocarbon activation processes.

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Vibrational spectra, force constants and conformations of molecules of trivalent tricoordinate phosphorus compounds

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Abstract. Data on the interpretation of the IR and Raman spectra based on normal coordinate analysis, on the force constants and on the conformations of the molecules of trivalent tricoordinate phosphorus compounds are summarised. The existing correlations between the spectra and molecular structures are refined and some new correlations are proposed. The bibliography includes 171 references.

I. Introduction

Vibrational spectroscopy is widely used in the chemistry of organophosphorus compounds for the identification of functional groups, determination of the molecular structure and studies on the molecular conformations, inter- and intramolecular interactions. Monographs by Thomas^{1,2} and atlases by Shagidullin *et al.*^{3–5} are devoted to the interpretation of IR spectra of organophosphorus compounds. Unfortunately, Raman spectroscopy has not become a routine method in phosphorus chemistry as yet, though the scope of possible application of this experimental technique in structural studies is as large as that of IR spectroscopy. This is to a great extent due to the lack of studies devoted to the generalisation of scarce information on the Raman spectra of different organophosphorus compounds. In this review, a comparative analysis is given of a continuously growing body of data on both the IR and Raman spectra of phosphorus-containing molecules. An attempt to summarise information on the ‘fingerprints’ of rotational isomerism in the molecules of tricoordinate phosphorus compounds as manifested in vibrational spectra is also undertaken.

A distinctive feature of the review is that here we consider only those molecules the spectra of which have been interpreted on the basis of normal coordinate analysis. A normal coordinate analysis

makes it possible to calculate the eigenvectors of normal vibrations, *i.e.*, to assess the contribution of each valence bond and each bond angle to a particular molecular vibration.^{6,7} This allows unambiguous assignment of the frequencies to the vibrations of particular structural fragments. Knowledge of the eigenvectors of normal vibrations is also necessary for the analysis of the interactions between vibrations of particular bonds in a molecule. It is known that effective coupling of vibrations of two molecular fragments is achieved if their individual frequencies are close ($\nu_1 \approx \nu_2$) and the fragments either share a number of atoms or are connected by a valence bond.⁸ For the coupling of vibrations to occur, they should also be of the same symmetry.⁹ As a result, coupling of two individual vibrations gives rise to two new coupled vibrations. Each fragment of the molecule makes a contribution to each of the new vibrations. Their frequencies (ν'_1 and ν'_2) can differ appreciably from the frequencies of the ‘old’ vibrations; as a rule, $\nu'_1 < \nu_1 \approx \nu_2 < \nu'_2$.

Thus in the molecule of methylphosphine (**1**), vibrations with a predominant contribution of the P–C bond occur at a frequency of about 670 cm^{–1}. Vibrations of two P–C bonds in the molecule of dimethylphosphine (**2**) give rise to two new vibrations, *viz.*, a symmetric stretch of both bonds at a frequency $\nu'_1 \approx 660$ cm^{–1} and an antisymmetric vibration at a frequency $\nu'_2 \approx 700$ cm^{–1}. These changes in the $\nu(\text{P–C})$ frequencies on going from molecule **1** to the molecule **2** are mainly due to the coupling of two individual oscillators sharing the phosphorus atom.

Vibrations of the PCl₂ group in the molecule of methyl phosphorodichloridite, CH₃OPCl₂ (**3**), are characterised by strong IR absorption bands at ~ 460 and ~ 500 cm^{–1}. The frequencies of bending vibrations of the butyl group lie in the same spectral region. However, analysis of the molecular structure of butyl phosphorodichloridite, C₄H₉OPCl₂, shows that these two vibrations cannot interact, since the structural fragments under consideration share no atoms and are not connected by a covalent bond. Therefore, vibrations of the PCl₂ group have identical patterns in the IR spectra of both C₄H₉OPCl₂ and CH₃OPCl₂.

These examples show that, strictly speaking, the lack of information on the eigenvectors of some vibrations makes it impossible to conclude whether they will be characteristic on going from one molecule to another. Therefore, spectral–struc-

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tural correlations become much more reliable if they are based on theoretical interpretation of the spectra.

A normal coordinate analysis also makes it possible to calculate the force constants of chemical bonds and bond angles in molecules. The force constants are primarily of interest as transferable parameters, which are used for calculating the vibrational spectra of related molecules.⁶ At the same time, they are also numerical characteristics of the potential surface of a molecule. It should be noted that for several reasons^{6,10} the force constant values depend on the type of computational procedures employed, so that small differences between the estimates of the force fields obtained by different authors for the same molecule are virtually inevitable. Because of this, here we compared the force constants assessed using the same approximations for series of related compounds. This makes it possible to judge the changes in the electronic structure of the molecules if analysis of their force fields reveals large and systematic deviations. The notations are given according to monograph⁶ and the values of force constants are given in 10^2 N m^{-1} .

Compounds of trivalent tricoordinate phosphorus were chosen to be the subject of this review primarily since they are most widely used in the syntheses of organophosphorus compounds. Additionally (probably, because of relatively low stability of tricoordinate phosphorus compounds), their vibrational spectra have been less studied than those of tetracoordinate phosphorus compounds. Virtually all results of normal coordinate analyses of vibrational spectra of organophosphorus compounds reported to date have been analysed. The exceptions are the results of studies on the simplest tetraatomic molecules of phosphine (PH_3) and its halogen derivatives ($\text{H}_n\text{PHal}_{3-n}$).

Spectral characteristics of all the compounds under discussion are listed in Tables. Each fundamental vibration was assigned a number as follows. The whole set of vibrations was divided into groups according to particular symmetry types of the vibrations. Within each symmetry type, the vibrations were numbered in descending order of their frequencies.

The frequencies assigned to overtones and combination bands are omitted. The notations of vibrations are ν for stretching, δ for bending, r for rocking, w for wagging, t for twisting and χ for torsional vibrations; γ denotes vibrations associated with the out-of-plane deviation of particular bonds. These notations describe the type of motion of particular structural fragments of molecules. In discussing any vibration of the entire molecule, that is, a simultaneous motion of several individual oscillators, the above-mentioned notations have a somewhat different meaning. For instance, the totally symmetrical fundamental vibration of the molecule **1** is composed of the contributions from not only the stretching vibrations $\nu(\text{P}-\text{C})$ of the $\text{P}-\text{C}$ bond, but also the wagging vibrations of the phosphino group, $w(\text{PH}_2)$. However, the major contribution to the energy of the resultant vibration is made by the $\text{P}-\text{C}$ bond; therefore, such a vibration is denoted below as $\nu(\text{P}-\text{C})$.

All frequencies are given in cm^{-1} . The intensities (I) and shapes of spectral bands, as well as the degree of depolarisation of the Raman lines (ρ), are qualitatively described using the following notations: w for weak, m for medium, s for strong, ms for medium strong, br for broad, v for very, sh for shoulder, p for polarised and dp for depolarised.

Spectral data listed in Tables are presented in the following order: the vibrational frequency (in cm^{-1}), a qualitative or quantitative description of the intensity (in the latter case, the intensity of a line with respect to that of the strongest Raman peak, taken as 100) and a qualitative or quantitative description of the degree of depolarisation.

II. Alkylphosphines

Vibrational spectra and conformations of primary alkylphosphines have been studied in most detail. Interpretation^{11–13} of the IR spectra¹¹ and the Raman spectra¹⁴ of methylphosphine

Table 1. Interpretation of vibrational spectra of methylphosphine.

No.	Symmetry	Assignment	Raman (l)	IR (g)
11	A''	$\nu_{\text{as}}(\text{PH}_2)$	2297, vs, p	2309, vs
3	A'	$\nu_{\text{s}}(\text{PH}_2)$	2297, vs, p	2305, vs
12	A''	$\delta_{\text{as}}(\text{CH}_3)$	~ 1440 , w	1435, m
4	A'	$\delta_{\text{as}}(\text{CH}_3)$	~ 1440 , w	1429, m
5	A'	$\delta_{\text{s}}(\text{CH}_3)$	1288, m, p	1296, w
6	A'	$\delta(\text{PH}_2)$	1086, m, p	1092, s
13	A''	$r(\text{CH}_3), t(\text{PH}_2)$		1017, m
7	A'	$r(\text{CH}_3), w(\text{PH}_2), \delta(\text{PH}_2)$	974, m, p	978, s
8	A'	$w(\text{PH}_2), r(\text{CH}_3), \nu(\text{P}-\text{C})$	740, s, p	730, w
14	A''	$t(\text{PH}_2), r(\text{CH}_3)$		696, w ^a
9	A'	$\nu(\text{P}-\text{C}), w(\text{PH}_2)$	673, s, p	676, s

Note. Hereafter, l stands for liquid and g for gas. Totally symmetric fundamental vibrations of the A' type were labelled with figures from 1 to 9 and antisymmetric vibrations of the A'' type were labelled with figures from 10 to 15. Vibrations with the highest frequency and belonging to the A' type (Nos 1 and 2) and A'' type (No. 10) and vibration No. 15 are not included, since they correspond to the $\text{C}-\text{H}$ stretching vibrations of the bonds, which are insignificant for analytical purposes. For the same reason, some vibrations are also not included in Tables 2–25.

^a Appears only in the spectrum of crystals.

(Table 1) and its D-isotopomers CH_3PD_2 , CD_3PH_2 and CD_3PD_2 has been given and the force constants have been estimated. Vibrational spectra of ethylphosphine (**4**) have been investigated in a number of studies.^{15–21} Using vibrational¹⁵ and microwave^{16,17} spectroscopy, the molecules of compound **4** were shown to exist in the liquid and gas phases in two rotameric forms, as *trans* (*T*) and *gauche* conformers (*G*) (Fig. 1; $\text{X} = \text{H}$,

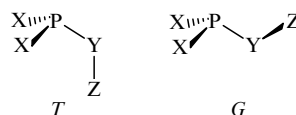


Figure 1. Conformers of molecules X_2PYZ : *trans* (*T*) and *gauche* (*G*).

$\text{Y} = \text{CH}_2$, $\text{Z} = \text{CH}_3$). Crystals of this compound are built of the molecules of the *trans* conformer only, so that the spectra are simplified owing to the disappearance of the bands of the *gauche* isomer. Interpretation of the spectra of ethylphosphine was based on the results of normal coordinate analysis²² performed simultaneously for both $\text{C}_2\text{H}_5\text{PH}_2$ and $\text{C}_2\text{H}_5\text{PD}_2$ molecules (Table 2). In studies of vibrational spectra of n-propylphosphine (**5**)²³ (Table 3) it has been shown that this compound exists in the liquid phase as a mixture of five conformers (Fig. 2; $\text{X} = \text{H}$, $\text{Y} = \text{CH}_2$). Vibrational and microwave spectra of isopropylphos-

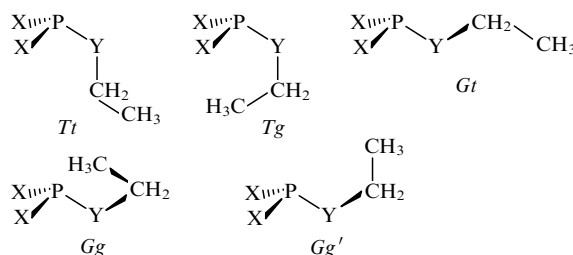


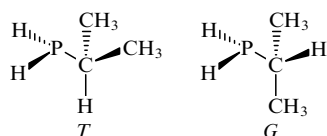
Figure 2. Conformers of molecules $\text{X}_2\text{PYCH}_2\text{CH}_3$: *trans,trans* (*Tt*), *trans,gauche* (*Tg*), *gauche,trans* (*Gt*), *gauche,gauche* (*Gg*) and *gauche,gauche'* (*Gg'*).

Table 2. Interpretation of vibrational spectra of ethylphosphine.

No.	Symmetry	Assignment	Raman (g)	IR (g)
17	A''	$\nu_{as}(\text{PH}_2)$		2304, vs
4	A'	$\nu_s(\text{PH}_2)$ 2298, vs	$\left\{ \begin{array}{l} 2296, \text{vs} \\ 2294, \text{vs} \end{array} \right.$	
8	A'	$w(\text{CH}_2), \nu_{as}(\text{PCC}), \delta(\text{CH}_2)$	1271, vw	
19	A''	$t(\text{CH}_2)$	1247, m	1247, w
9	A'	$\delta(\text{PH}_2), \nu(\text{C}-\text{C}), w(\text{PH}_2)$	1086, w	1085, m
10	A'	$\nu(\text{C}-\text{C}), \delta(\text{PH}_2)$	1065, m, sh	1067, m
20	A''	$r(\text{CH}_3), r(\text{CH}_2), t(\text{PH}_2)$	1056, m	1055, m
11	A'	$r(\text{CH}_3), w(\text{CH}_2), \delta(\text{PCC})$	982, w	979, w
21	A''	$t(\text{PH}_2), r(\text{CH}_3), r(\text{CH}_2)$	835, w	833, m
12	A'	$w(\text{PH}_2), w(\text{CH}_2), \delta(\text{CH}_2), \delta(\text{PH}_2)$	818, m	817, m
22	A''	$r(\text{CH}_2), t[\text{PH}_2(G)]$	692, m	
		$r(\text{CH}_2), t(\text{PH}_2)$	640, vs	643, w
13	A'	$\nu(\text{P}-\text{C}), \delta(\text{PCC})$	636, vs	634, w
14	A'	$\delta(\text{PCC})$	307, m	
		$\delta[\text{PCC}(G)]$	288, w	
23	A''	$\chi(\text{CH}_3), \chi(\text{PH}_2)$		245, w
24	A''	$\chi(\text{PH}_2), \chi(\text{CH}_3)$		183, w
		$\chi[\text{PH}_2(G)]$	162, vw	

Note. The number of vibration, symmetry type and assignment are given for the *T* conformer (see Fig. 1). Lines of the *G* conformer were interpreted only if they did not coincide with the corresponding lines of the *T* conformer (their assignments are denoted by the character 'G').

phine (**6**) and its D-isotopomer, iso- $\text{C}_3\text{H}_7\text{PD}_2$, have been studied.^{24,25} It was shown that the *G* and *T* conformers of these molecules are stable in the liquid and gas phases.



The calculated assignments²² for isopropylphosphine **6** (see Table 4) are somewhat different from the empirical ones.²⁴

Compared with the spectra of primary alkylphosphines, the interpretation of the spectra of secondary and tertiary alkylphosphines is more complicated because of the necessity to take into account the coupling of vibrations of adjacent alkyl groups at the phosphorus atom. Therefore, it is not surprising that the spectra of such simple representatives of organophosphorus compounds as dimethylphosphine and its isotopomers have been interpreted in different ways.^{26–29} The problem of contradictory assignments was alleviated only after performing a normal coordinate analysis.^{12,13,29} Different versions of empirical interpretation of the vibrational spectra of phosphirane $(\text{CH}_2)_2\text{PH}$ (**7**) and its deuterio derivatives have also been suggested.^{30,31} Calculations³² made it possible to refine the vibrational assignments and to assess the force constants of the molecule, its thermodynamic functions and the barrier to inversion of the phosphirane ring.

Trimethylphosphine (**8**) is the first organophosphorus compound for which a normal coordinate analysis has been performed.³³ The data on both the eigenvectors of molecular vibrations of $(\text{CH}_3)_3\text{P}$ and $(\text{CD}_3)_3\text{P}$ and the force fields of the molecules have been repeatedly revised.^{13,14,34–40} These molecules have a C_{3v} symmetry, therefore the A_2 modes are optically inactive and not observed in the spectra. Some of the modes were observed owing to the reduction of symmetry of the molecule as a result of crystallisation of the substance.³⁹ Nevertheless, a number of vibrational assignments had to be revised after the spectra of low-symmetric D-isotopomers, $(\text{CH}_3)_2\text{CD}_3\text{P}$ and $\text{CH}_3(\text{CD}_3)_2\text{P}$, had been reported.⁴¹ The force constants of the molecule **8** have

Table 3. Interpretation of vibrational spectra of n-propylphosphine.

No.	Symmetry	Assignment	Raman (l)	IR (g)
5	A'	$\nu_s[\text{PH}_2(Tg, Gg')]$	2300, sh, p	2306, s ^a
		$\nu_s(\text{PH}_2)$	2289, sh, p	2298, vs
23	A''	$\nu_{as}(\text{PH}_2)$	2285, vs, p	2294, vs
11	A'	$w(\text{CH}_2\text{P})$	1228, m, p	1233, sh ^a
26	A''	$t(\text{CH}_2\text{P}), r(\text{CH}_3), r(\text{CH}_2)$	1218, m, p	1221, w ^a
		$t[\text{CH}_2\text{P}(Gg, Gg')]$	1203, sh, p	1207, sh
12	A'	$\delta(\text{PH}_2)$	1097, m, p	1104, sh
		$\delta[\text{PH}_2(Gt, Gg')]$	1094, m, p	1096, w ^a
13	A'	$r(\text{CH}_3), \nu_s(\text{CCC})$	1075, m, p	1085, s
27	A''	$r(\text{CH}_3), t(\text{CH}_2\text{P}), t(\text{PH}_2), t(\text{CH}_2)$	1061, w ^b	1073, m ^a
		$r(\text{CH}_3), t[\text{CH}_2\text{P}(Gg, Gg')]$	1052, w ^c	1052, sh
14	A'	$\nu_{as}(\text{CCC})$	1032, m, p	1037, sh
28	A''	$t(\text{PH}_2)$	907, vw, p	910, sh
		$t(\text{PH}_2), r(\text{CH}_3), \nu_s[\text{CCC}(Gt)]$	898, m, p	898, m
		$t(\text{PH}_2), \nu_s[\text{CCC}(Gg')]$	880, m, p	883, sh
15	A'	$\nu_s(\text{CCC}), r(\text{CH}_3), t(\text{PH}_2)$	898, m, p	898, m
		$\nu_s(\text{CCC}), w(\text{PH}_2), \nu[\text{P}-\text{C}(Tg)]$	846, m ^c	845, m
		$\nu_s(\text{CCC}), t(\text{PH}_2), \nu[\text{P}-\text{C}(Gt)]$	812, vw, dp	812, sh
		$w(\text{PH}_2), r(\text{CH}_3), r(\text{CH}_2\text{P}), \nu_s[\text{CCC}(Gt)]$	889, m, p	891, sh
		$w(\text{PH}_2), \nu_s[\text{CCC}(Tg, Gg)]$	880, m, p	883, sh
16	A'	$w(\text{PH}_2), \nu_s(\text{CCC}), \nu(\text{P}-\text{C})$	840, m, p	838, m ^a
29	A''	$r(\text{CH}_2), r(\text{CH}_3), t(\text{PH}_2)$	768, w, p	770, m
		$\nu[\text{P}-\text{C}(Gt)]$	704, s, p	700, vw ^a
17	A'	$\nu(\text{P}-\text{C}), w(\text{PH}_2), \delta(\text{CCC})$	676, s, p	680, m
		$\nu[\text{P}-\text{C}(Gg')]$	636, sh, p	640, sh
		$\nu[\text{P}-\text{C}(Gg)]$	628, sh, p	
		$\nu[\text{P}-\text{C}(Tg)]$	624, s, p	625, m
30	A''	$r(\text{CH}_2\text{P}), t(\text{PH}_2)$	648, w ^c	647, w ^c
18	A'	$\delta(\text{CCC}), \nu(\text{P}-\text{C}), \delta(\text{PCC})$	357, s, p	355, s
		$\delta(\text{CCC}), \nu(\text{P}-\text{C}), \delta(\text{PCC}), \nu_s[\text{CCC}(Gt)]$	348, m ^b	348, s
		$\chi(\text{C}-\text{CH}_3), \chi(\text{P}-\text{C}), \chi[\text{C}-\text{C}_2\text{H}_5(Tg, Gg')]$	284, w, p	285, w
		$\chi(\text{C}-\text{CH}_3), \delta(\text{PCC}), \chi[\text{C}-\text{C}_2\text{H}_5(Gg)]$	268, sh ^b	
31	A''	$\chi(\text{C}-\text{CH}_3)$		239, w
19	A'	$\delta(\text{PCC}), \delta(\text{CCC})$	230, w, p	227, sh
		$\delta(\text{PCC}), \delta[\text{CCC}(Gt)]$	215, vw ^b	215, sh
32	A''	$\chi(\text{P}-\text{C})$	214, vw ^c	185.4, s
		$\chi[\text{P}-\text{C}(Gt)]$		177, s
33	A''	$\chi(\text{C}-\text{C}_2\text{H}_5)$	126, vw ^c	105, m

Note. The number of vibration, symmetry type and assignment are given for the *Tt* conformer (see Fig. 2). Vibrations of other conformers (for notations of their frequencies, see Caption to Fig. 2) were interpreted only if their frequencies did not coincide with the corresponding lines of the *Tt* conformer.

^a From the spectrum of n-propylphosphine solution in liquid krypton.

^b From the gas-phase spectrum.

^c From the low-temperature spectrum of solid n-propylphosphine.

been re-calculated^{42–44} using the results of *ab initio* quantum-chemical calculations; it should be mentioned that not only the spectra of deuterated specimens, but also those of ¹³C-isotopomers of trimethylphosphine **8** have been analysed⁴³ and that vibrational anharmonicity has also been taken into account.

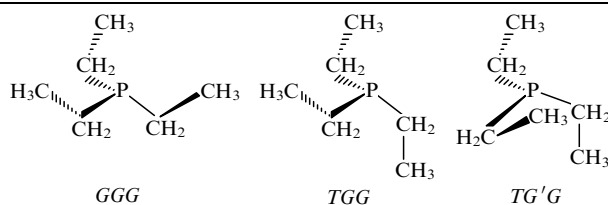
The molecule of triethylphosphine (**9**) can adopt four conformations;⁴⁵ however, it has been shown^{45,46} that vibrational spectra of compound **9** in the liquid phase (see Refs 46, 47) can be interpreted assuming the existence of only three conformers shown below.

Table 4. Interpretation of vibrational spectra of isopropylphosphine.

No.	Symmetry	Assignment	Raman (g)	IR (g)
22	A''	$\nu_{as}[\text{PH}_2(G)]$	2299, vs	2299, vs
		$\nu_{as}(\text{PH}_2)$		2288, vs
5	A'	$\nu_s[\text{PH}_2(G)]$	2297, vs	2297, vs
		$\nu_s(\text{PH}_2)$	2286, vs	
9	A'	$\delta(\text{CH}), w(\text{PH}_2)$	1255, m	1256, m
26	A''	$r(\text{CH}), \nu_{as}(\text{CC}_2), r(\text{CH}_3)$	1237, w	1234, w
		$r(\text{CH}), \nu_{as}(\text{CC}_2), r[\text{CH}_3(G)]$	1231, w	
27	A''	$\nu_{as}(\text{CC}_2), r(\text{CH})$	1164, vw	
10	A'	$r(\text{CH}_3), \delta(\text{CH}), \nu_s(\text{CC}_2)$	1114, m	
11	A'	$\delta(\text{PH}_2)$	1077, m	
12	A'	$r(\text{CH}_3), \nu(\text{P}-\text{C}), w(\text{CC}_2), \delta(\text{PH}_2)$	1067, m	1066, s
28	A''	$r(\text{CH}_3)$	$\sim 970^a$	$\sim 970^a$
29	A''	$r(\text{CH}_3), \delta(\text{CH})$		924, vw
13	A'	$\nu_s(\text{CC}_2), r(\text{CH}_3), \delta(\text{CH})$	892, m	892, w
		$w(\text{PH}_2), \delta[\text{CH}(G)]$	813, m	813, s
14	A'	$w(\text{PH}_2), \delta(\text{CH})$	792, w	791, s
30	A''	$t(\text{PH}_2)$		809, m
		$\nu(\text{P}-\text{C}), w(\text{CC}_2), \delta[\text{CC}_2(G)]$	628, m, sh	626, vw
15	A'	$\nu(\text{P}-\text{C}), w(\text{CC}_2), \delta(\text{CC}_2)$	606, s	606, w
16	A'	$\delta(\text{CC}_2), \chi(\text{CH}_3)$		388, w
17	A'	$w(\text{CC}_2), \chi(\text{CH}_3)$	325, m	325, w
		$w(\text{CC}_2), \chi[\text{CH}_3(G)]$	309, vw	
31	A''	$r(\text{CC}_2), \chi(\text{CH}_3)$	322, w, sh	322, w
18	A'	$\chi(\text{CH}_3)$		287, w
32	A''	$\chi(\text{CH}_3)$		266, vw, br
33	A''	$\chi(\text{P}-\text{C})$	163, vw	163, s

Note. The number of vibration, symmetry type and assignment are given for the *T* conformer. The lines of the *G* conformer (denoted by character 'G') were interpreted only if their frequencies did not coincide with the corresponding lines of the *T* conformer.

^a The frequency was suggested after normal coordinate analysis²² (was not observed experimentally).



The *GGG* and *TG'G* conformers are present simultaneously in the crystalline phase.^{45,46} Theoretical interpretation of the spectra^{46,47} of triethylphosphine **9** was based on the results of normal coordinate analysis⁴⁵ performed using the force constants for molecules **8** and **4**.

Comparison of the spectra of primary alkylphosphines reveals three vibrations, *viz.*, the $\nu_{as}(\text{PH}_2)$, $\nu_s(\text{PH}_2)$ and $\delta(\text{PH}_2)$ ones, which seem to be the most characteristic vibrations of these compounds. The first two vibrations appear as two very strong bands with similar frequencies near $\sim 2300 \text{ cm}^{-1}$ in the gas-phase spectra. On going from gases to liquids, these bands usually coalesce into one band observed in the frequency range $2275\text{--}2300 \text{ cm}^{-1}$ (see, *e.g.*, Refs 15, 18–20, 23, 24, 48, 49). A normal coordinate analysis shows that the vibrations $\nu_{as}(\text{PH}_2)$ and $\nu_s(\text{PH}_2)$ are the characteristic vibrations, *i.e.*, that the frequencies and intensities of the corresponding spectral peaks are determined solely by the properties of the $\text{P}-\text{H}$ bonds.

Scissoring vibrations of the phosphino group, $\delta(\text{PH}_2)$, can mix to a certain degree with vibrations of the alkyl radical (see, *e.g.*, Table 2), which affects mainly the intensities of corresponding bands. At the same time, the frequency of the $\delta(\text{PH}_2)$ vibration depends only slightly on the vibration of the alkyl fragment of the molecule and lies in a relatively narrow frequency range between 1073 and 1097 cm^{-1} (for liquids).^{15, 18–20, 23, 24, 48, 49} Mixing of the

scissoring deformation vibration $\delta(\text{PH}_2)$ with the wagging vibration $w(\text{PH}_2)$ also occurs (see Table 2). Probably, that is why the former vibration has been interpreted²⁰ as $w(\text{PH}_2)$.

The structure of the alkyl fragments of the molecules of primary alkylphosphines strongly affects the frequency of vibration with predominant contribution of the $\text{P}-\text{C}$ bond (Tables 1–5). For instance, the frequency of the vibration

Table 5. Stretching vibrations of $\text{P}-\text{C}$ bonds in the spectra of alkylphosphines and their substituted derivatives.

Molecule	Assignment	Raman	IR
CH_3PH_2	$\nu(\text{P}-\text{C}), w(\text{PH}_2)$	673, w, p (l)	676, s (g)
CH_3PCl_2	$\nu(\text{P}-\text{C}), \delta_s(\text{CH}_3)$	691, w, p (l)	690, s (cr)
CH_3PF_2	$\nu(\text{P}-\text{C}), w(\text{PF}_2), \delta_{as}(\text{CH}_3)$	709, w, p (l)	727, w (cr), 711, m (cr)
$\text{C}_2\text{H}_5\text{PH}_2$	$\nu(\text{P}-\text{C}), \delta(\text{PCC})$	636, vs (g)	634, w (g)
$\text{C}_2\text{H}_5\text{PCl}_2$	$\nu(\text{P}-\text{C}), \delta[\text{CCP}(G)]$	663, m, p (l)	666, s (g)
	$\nu(\text{P}-\text{C}), \delta[\text{CCP}(T)]$	631, m, p (l)	632, m (g)
$\text{C}_2\text{H}_5\text{PF}_2$	$\nu[\text{P}-\text{C}(G)]$	682, m, p (g)	680, s (g)
	$\nu(\text{P}-\text{C}), \delta(\text{CCP}),$ $w[\text{CH}_2(T)]$	655, s, p (g)	651, m (g)
$n\text{-C}_3\text{H}_7\text{PH}_2$	$\nu[\text{P}-\text{C}(G)]$	704, w, p (l)	700, w (s)
	$\nu(\text{P}-\text{C}), w(\text{PH}_2),$ $\delta[\text{CCC}(T)]$	676, w, p (l)	680, m (g)
	$\nu[\text{P}-\text{C}(Gg')]$	636, sh, p (l)	640, sh (g)
	$\nu[\text{P}-\text{C}(Gg)]$	628, sh, p (l)	
	$\nu[\text{P}-\text{C}(Tg)]$	624, w, p (l)	625, m (g)
$n\text{-C}_3\text{H}_7\text{PCl}_2$	$\nu[\text{P}-\text{C}(G)]$	736, w, p (l)	738, w (g)
	$\nu(\text{P}-\text{C}), \delta(\text{CCC}),$ $\delta[\text{CCP}(Tr)]$	687, w, p (l)	690, w (g)
	$\nu(\text{P}-\text{C}), r[\text{CH}_2(Gg')]$	650, w, p (l)	650, w (g)
$\text{iso-C}_3\text{H}_7\text{PH}_2$	$\nu(\text{P}-\text{C}), w(\text{CC}_2),$ $\delta[\text{CC}_2(G)]$	628, m, sh (g)	626, vw (g)
	$\nu(\text{P}-\text{C}), w(\text{CC}_2),$ $\delta[\text{CC}_2(T)]$	606, s (g)	606, w (g)
$(\text{CH}_3)_2\text{PH}$	$\nu_{as}(\text{PC}_2)$	704, (g)	704.5, s (g)
	$\nu_s(\text{PC}_2)$	660, m, p (g)	{ 667, w (g) 660, w (g)}
$(\text{CH}_2)_2\text{PH}$	$w(\text{CH}_2), \text{ring 'breating',}^a$ $r(\text{PH}), \text{symmetric}$ deformation^b $t(\text{CH}_2), r(\text{CH}_2), \text{non-sym-}$ $\text{metric deformation}^c$ $r(\text{PH})$	1056, s, p (g)	1058, vs (g)
$(\text{CH}_3)_2\text{PCl}$	$\nu_{as}(\text{PC}_2)$	708, m, dp (l)	707, s (l)
	$\nu_s(\text{PC}_2)$	674, w, p (l)	675, s (l)
$(\text{CH}_3)_3\text{P}$	$\nu_{as}(\text{PC}_3)$	708, m, dp (g)	{ 716, m (g) 709, m (g) 706, m (g)}
	$\nu_s(\text{PC}_3)$	653, vs, p (g)	
$(\text{C}_2\text{H}_5)_3\text{P}$	$\nu_{as}(\text{PC}_3), \delta[\text{PCC}(TGG')]$ ^d	697, m (l)	690, s (l)
	$\nu_{as}(\text{PC}_3),$ $\delta[\text{PCC}(GGG, TGG)]$	669, s (l)	670, m (l)
	$\nu_{as}(\text{PC}_3)^c$		659, m (l)
	$\nu_s(\text{PC}_3), \delta[\text{PCC}(GGG)]$		625, m (l)
	$\nu_s(\text{PC}_3), \delta[\text{PCC}(TGG')]$	619, vs (l)	619, m (l)
	$\nu_s(\text{PC}_3), \delta[\text{PCC}(TGG)]$		600 m (l)

Note. Notations: cr stands for crystal and s for solution (in Kr).

^a Ring 'breating' vibration accompanied by synchronous changes in the $\text{P}-\text{C}$ and $\text{C}-\text{C}$ bond lengths.

^b Symmetric ring deformation accompanied by synchronous lengthening of two $\text{P}-\text{C}$ bonds and shortening of the $\text{C}-\text{C}$ bond.

^c Non-symmetric ring deformation associated with $\nu_{as}(\text{PC}_2)$.

^d Vibrations of the *A'* symmetry type.

^e Vibrations of the *A''* symmetry type.

$\nu(\text{P}-\text{C})$ decreases by $\sim 70 \text{ cm}^{-1}$ on going from the molecule **1** to the molecule **6** (see Tables 1 and 4). According to calculations, this is due to not only the 'weighting' of the alkyl group, but also a decrease in the force constant $K_{\text{P}-\text{C}}$.

The $\nu(\text{P}-\text{C})$ vibration can mix with deformation vibrations of the phosphino group and alkyl radical. Because of the changes in the contributions of particular groups to the vibrations, the intensities of the corresponding bands in the IR spectra can vary over a wide range on going from one alkylphosphine to another, which severely hampers their assignment. It is much easier to use the Raman spectra for identification of the vibration $\nu(\text{P}-\text{C})$, since the corresponding lines in the spectra of compounds in question always are the most intense and polarised in the frequency range $550-705 \text{ cm}^{-1}$. Thus, it is the Raman spectra that should be used for easy discrimination between different primary alkylphosphines.

When assigning the $\nu(\text{P}-\text{C})$ vibration, it should be remembered that the corresponding frequency can be 'sensitive' to molecular conformations. Therefore, a number of 'extra' peaks is often observed in the vibrational spectra of compounds, whose molecules can adopt several conformations (see, e.g., Tables 2 and 5). Some of the 'extra' peaks disappear as a result of crystallisation of the specimens.

Like the $\nu(\text{P}-\text{H})$ vibrations of primary alkylphosphines, those of the secondary alkylphosphines are observed in nearly the same spectral region $2270-2298 \text{ cm}^{-1}$. On the other hand, lines corresponding to two (rather than one) stretching vibrations of the $\text{P}-\text{C}$ bonds are observed in the spectra of secondary phosphines (see Table 5). An intense, strongly polarised Raman line observed in the region $550-670 \text{ cm}^{-1}$ is associated with symmetric $\nu_s(\text{PC}_2)$ vibrations, while a somewhat weaker and weakly polarised line in the region $600-710 \text{ cm}^{-1}$ is attributed to antisymmetric $\nu_{as}(\text{PC}_2)$ vibrations. In the IR spectra, the latter band is usually stronger than the former. As for the primary phosphines, the $\nu(\text{P}-\text{C})$ frequencies are, as a rule, 'conformationally sensitive' and decrease substantially as the chain length of alkyl radicals increases. All the aforesaid refers to acyclic dialkylphosphines and unstrained cyclic systems. Closure of three-, four- and five-membered strained rings leads to an increase in the $\nu_s(\text{PC}_2)$ frequencies, so that they become higher than the $\nu_{as}(\text{PC}_2)$ frequencies and lie beyond the upper bounds of the corresponding spectral regions.

The $\nu_s(\text{PC}_3)$ and $\nu_{as}(\text{PC}_3)$ stretching vibrations of the $\text{P}-\text{C}$ bonds in the molecules of tertiary phosphines have spectral features similar to those mentioned above (see Table 5). Since the lines corresponding to some characteristic vibrations such as $\nu(\text{P}-\text{H})$ or $\delta(\text{PH}_2)$ are absent in this case, identification of the spectra of tertiary phosphines should be performed using both the $\nu_s(\text{PC}_3)$ and $\nu_{as}(\text{PC}_3)$ lines and the alkyl group bands. The frequencies of some vibrations of the methyl or ethyl radicals at the phosphorus atom are sufficiently characteristic, which makes it possible to use them in the spectral analysis. For instance, the bands associated with symmetrical $\delta_s(\text{CH}_3\text{P})$ and antisymmetrical $\delta_{as}(\text{CH}_3\text{P})$ deformation vibrations are observed in the IR spectra of any liquid alkylphosphines in the regions $\sim 1280-1295$ and $\sim 1410-1445 \text{ cm}^{-1}$, respectively. The $\nu(\text{CH}_3\text{P})$ rocking vibrations mix with vibrations of other groups at the phosphorus atom (see Table 1). Changes in the environment around the P atom lead to substantial changes in the frequency and eigenvector of the resultant complex vibration. Therefore, the corresponding bands in the IR spectra of liquid alkylphosphines are observed in a rather wide region between 940 and 985 cm^{-1} and their intensities can vary from weak to strong. In the Raman spectra of alkylphosphines, the lines attributed to all the three vibrations are usually of weak or medium intensity.

If the ethyl radical is bound to the phosphorus atom, the $\delta(\text{CH}_2)$ bending and $\nu(\text{CH}_2)$ twisting vibrations of the methylene group can be considered characteristic. The corresponding peaks in vibrational spectra are usually of medium intensity and observed in the spectral regions $\sim 1410-1430$ and

$\sim 1230-1250 \text{ cm}^{-1}$, respectively. A complex vibration with predominant contribution of the wagging motion, $w(\text{CH}_2)$, is characterised by a slightly higher frequency ($\sim 1240-1280 \text{ cm}^{-1}$). Since this vibration is strongly coupled, the intensity of the corresponding peak can vary from very weak to medium. On the contrary, vibrations of the $\text{C}-\text{C}$ bond are characteristic and associated with rather strong peaks in the region $\sim 1020-1065 \text{ cm}^{-1}$. Rocking and wagging vibrations of the methylene group mix with the motions of other atoms constituting the alkylphosphine molecule and usually give rise to several peaks in the spectral region $\sim 690-820 \text{ cm}^{-1}$. At least one of the peaks is of rather high intensity.

It should be noted that the above-mentioned frequencies are specific to not only alkylphosphines, but also other organophosphorus compounds,¹⁻⁵ the molecules of which contain the CH_3P or $\text{C}_2\text{H}_5\text{P}$ fragments. This specificity is due to both the mass of the phosphorus atom and the peculiarities of the electronic structure of these fragments, which affect the force constant values. Bands corresponding to the bending and twisting vibrations of the methylene group at the phosphorus atom of an arbitrary coordination are observed in the spectral regions $\sim 1430-1380$ and $\sim 1190-1220 \text{ cm}^{-1}$, respectively, and can be used for the identification of non-branched alkylphosphorus groups. It is more convenient to use the Raman spectra for identification of twisting vibrations, since the corresponding bands in the IR spectra are often weak.

The above-mentioned frequency ranges for the 'fingerprint' bands are given for the liquid-phase spectra, since they are most widely used in routine studies. However, these spectral regions are only slightly shifted on going to the spectra of gases and crystals. For alkylphosphines, the shifts of spectral peaks due to the change in the state of aggregation usually do not exceed $10-15 \text{ cm}^{-1}$. The band intensities also vary only slightly, which indicates the absence of strong intermolecular interactions in the condensed phases. It should be taken into account that crystallisation of alkylphosphines, whose molecules can adopt several conformations, can lead to disappearance of some spectral bands.

III. Alkyl(halogeno)phosphines

Almost no interactions between the vibrations involving relatively heavy halogen atoms and light hydrogen atoms occurs in the molecules of alkyl(halogeno)phosphines. Therefore, skeletal vibrations in these compounds are much less 'sensitive' to substitution of deuterium atoms for hydrogen atoms, so that deuteration, which often facilitates the interpretation of the spectra, appears to be ineffective. Strengthening of intermolecular interactions due to the presence of halogen atoms in the molecules is yet another objectionable circumstance. This can cause shifts of spectral peaks comparable in magnitudes with those caused by structural rearrangement, which precludes the interpretation of experimental results.

Comparison of the spectral characteristics of the $\text{P}-\text{F}$ stretching vibrations for different states of aggregation of difluoro(methyl)phosphine (**10**)^{50,51} makes it possible to assess the effect of intermolecular interactions on these vibrations (Table 6). Vibrational spectra of compound **10** and dichloro(methyl)phosphine (**11**)⁵²⁻⁵⁶ have been interpreted.^{51,56,57} The results obtained in the two last-mentioned studies differ mainly in the assignment of the ν_8 and ν_9 frequencies. In Ref. 57, they were assigned to the vibrations $\delta(\text{PCl}_2)$ and $w(\text{PCl}_2)$, respectively, while the opposite assignment has been given in Ref. 56. The latter attribution is in better agreement with the vibrational assignments for the molecule $\text{C}_2\text{H}_5\text{PCl}_2$ (**12**) based on the results of *ab initio* quantum-chemical calculations.⁵⁸

Difluoro(ethyl)phosphine (**13**) and dichloro(ethyl)phosphine exist in the gas and liquid phases as mixtures of the *T* and *G* conformers^{21,56,58-60} (see Fig. 1; $\text{X} = \text{F}, \text{Cl}$; $\text{Y} = \text{CH}_2$; $\text{Z} = \text{CH}_3$). Vibrational spectra of the former substance and its deuterio derivative have been interpreted⁶⁰ and it was shown that

Table 6. Characteristic frequencies of the stretching vibrations of PF₂ bonds in the spectra of several organophosphorus compounds.

Molecule	Assignment	Raman	IR
CH ₃ PF ₂	$\nu_s(\text{PF}_2)$, $r(\text{CH}_3)$	812, w, p (g)	
		795, w, p (l)	
		789, w (cr)	798, s (cr)
	$\nu_{as}(\text{PF}_2)$, $r(\text{CH}_3)$	800, w, dp (g)	
		769, w, dp (l)	
C ₂ H ₅ PF ₂	$\nu_s(\text{PF}_2)$	755, w (cr)	767, s (cr)
	$\nu_{as}(\text{PF}_2)$, $r(\text{CH}_2)$	819, m, p (g)	830, vs (g)
	$\nu_{as}(\text{PF}_2)$, $r(\text{CH}_2)$	796, w, dp (g)	819, vs (g)
ClCH ₂ PF ₂	$\nu_s(\text{PF}_2)$, $\nu(\text{CCl})$, $\nu(\text{P}-\text{C})$	849, m, p (l)	859, vs (g)
	$\nu_s(\text{PF}_2)$, $\nu(\text{CCl})$, $\nu[\text{P}-\text{C}(G)]$	790, m, p (l)	826, vs (g)
	$\nu_{as}(\text{PF}_2)$, $r(\text{CH}_2)$	813, sh (l)	799, s (g)
CF ₃ PF ₂	$\nu_s(\text{PF}_2)$	861, m, p (g)	864, s (g)
	$\nu_{as}(\text{PF}_2)$	850, m, dp (g)	848, sh, w (g)

crystallisation of the specimens leads to the 'freezing out' of the *gauche* conformers. Unlike difluoro(ethyl)phosphine, both conformers of dichloro(ethyl)phosphine exist in the crystalline state.^{21, 56} Vibrational spectra of C₂H₅PCl₂ (see Refs 21, 56) and C₂D₅PCl₂ (see Ref. 21) have been analysed repeatedly.^{21, 56, 58} It is believed that comparison of the results obtained in the *ab initio* calculations⁵⁸ of the vibrations of heavy atoms of molecule C₂H₅PCl₂ with assignments²¹ of the vibrations with predominant contribution of hydrogen atoms provides a version of the interpretation of the spectra of compounds **12**, which does not contradict experimental results^{21, 56, 58} (Table 7).

The molecule of dichloro(propyl)phosphine, n-C₃H₇PCl₂ (**14**), can adopt five stable conformations (see Fig. 2; X = Cl, Y = CH₂). Analysis of the vibrational spectra of compound **14** showed⁶¹ that the *Tt*, *Gt* and *Gg'* conformers exist in the liquid phase. The interpretation of the spectra of dichloro(propyl)phos-

Table 7. Interpretation of vibrational spectra of dichloro(ethyl)phosphine.

No.	Symmetry	Assignment	Raman (l) ^a	IR (g) ^a
8	A'	$\nu(\text{CC})$	1038, w, p	1040, m
		$\nu[\text{CC}(G)]$	1022, w, p	1026, m
9 ^b	A'	$r(\text{CH}_3)$, $\delta(\text{CCP})$	990, vw, p	994, w
19 ^b	A''	$r(\text{CH}_3)$, $r(\text{CH}_2)$	975, vw, dp	976, vw
		$r(\text{CH}_2)$, $r[\text{CH}_3(G)]$	750, vw, p	752, s
20	A''	$r(\text{CH}_2)$, $r(\text{CH}_3)$	727, vw, dp	728, m
		$\nu(\text{P}-\text{C})$, $\delta[\text{CCP}(G)]$	663, m, p	666, s
10	A'	$\nu(\text{P}-\text{C})$, $\delta(\text{CCP})$	631, m, p	632, m
11	A'	$\nu_s(\text{PCl}_2)$, $\delta(\text{CCP})$	499, vs, p	506, vs
21	A''	$\nu_{as}(\text{PCl}_2)$	478, s, p	498, vs
12	A'	$\delta(\text{CCP})$, $\nu_s(\text{PCl}_2)$	400, m, p	403, s
		$\delta[\text{PCl}_2(G)]$	320, m, p	321, m
13	A'	$\delta(\text{PCl}_2)$	213, m, p	213, m
22	A''	$t(\text{PCl}_2)$	191, m, dp	185, s
		$t[\text{PCl}_2(G)]$	165, w, p	156, w
		$w[\text{PCl}_2(G)]$	286, m, p	287, s
14	A'	$w(\text{PCl}_2)$	178, w, p	175, s, sh
23	A''	$\chi(\text{CH}_3)$		184, w
		$\chi[\text{CH}_3(G)]$		180, w
24	A''	$\chi(\text{PCl}_2)$	113, w	
			83, vw ^c	

^a Vibrations with frequencies higher than 1200 cm⁻¹ are not listed.

^b The reverse assignment of the ν_9 and ν_{19} vibrations has also been reported.¹⁸

^c From the gas-phase spectrum.

Table 8. Interpretation of vibrational spectra of dichloro(chloromethyl)phosphine.

No.	Symmetry	Assignment	Raman (l)	IR (g)
12	A''	$r(\text{CH}_2)$, $t[\text{CH}_2(G)]$	812, w	816, m
4	A'	$r(\text{CH}_2)$	776, vw, p	774, sh
		$\nu(\text{CCl})$, $\delta(\text{PCCl})$, $\nu[\text{P}-\text{C}(G)]$	746, w	757, m
		$\nu(\text{P}-\text{C})$, $\delta(\text{PCCl})$, $\delta(\text{CH}_2)$, $\delta[\text{PCl}_2(G)]$	683, s, p	688, s
5	A'	$\nu(\text{P}-\text{C})$	620, vw, p	623, vw
13	A''	$\nu_{as}(\text{PCl}_2)$, $\nu_s[\text{PCl}_2(G)]$	494, vs	508, vs
6	A'	$\nu_s(\text{PCl}_2)$, $\nu_{as}[\text{PCl}_2(G)]$	494, vs, p	498, vs
7	A'	$\delta(\text{PCCl})$	364, vw	365, w
		$\delta(\text{PCCl})$, $\delta(\text{PCl}_2)$, $w(\text{CH}_2)$, $t[\text{PCl}_2(G)]$	274, w	274, vs
		$w(\text{PCl}_2)$, $\delta(\text{PCl}_2)$, $\nu_s[\text{PCl}_2(G)]$	256, vs, p	256, vs
8	A'	$w(\text{PCl}_2)$	228, vw	
14	A''	$\delta(\text{PCl}_2)$	203, w, p	
		$t(\text{PCl}_2)$, $\delta(\text{PCCl})$, $w[\text{CH}_2(G)]$	143, w	136, s
9	A'	$\delta(\text{PCl}_2)$, $\nu(\text{P}-\text{C})$, $\delta(\text{PCCl})$, $w[\text{CH}_2(G)]$	187, s	187, s
15	A''	$\chi(\text{P}-\text{C})$	90, vw	85, w

Note. The number of vibration, symmetry species and tentative vibrational assignments are given for the *T* conformer only. Detailed assignment is given for the *G* conformer only.

phine was based on the results of *ab initio* quantum-chemical calculations.⁶¹

The molecules of (chloromethyl)difluorophosphine ClCH₂PF₂ (**15**) and (chloromethyl)dichlorophosphine ClCH₂PCl₂ (**16**) exist^{62–65} both in the liquid and gas phases as mixtures of the *T* and *G* conformers (see Fig. 1; X = F, Cl; Y = CH₂; Z = Cl). Crystallisation of these substances leads to the 'freezing out' of one isomeric form, so that the crystals of compound **16** comprise the molecules of only the *gauche* conformer,⁶⁴ while the molecules of compound **15** comprise the *trans* conformer.⁶³ The spectra of both compounds were interpreted using the force fields obtained from normal coordinate analysis for the corresponding deuterio derivatives.^{63, 64} The assignments suggested⁶⁴ for compound **16** (Table 8) differ from those given earlier,^{56, 66} which is likely due to impurities present in the specimens studied.^{56, 66}

In studying the vibrational spectra of (CH₃)₂PCl (**17**) it has been shown^{49, 67} that the molecules of this compound form asymmetrical dimers in the crystals. This leads to the doublet splitting of a large number of singlet (in the spectra of liquid) bands and lines (Table 9). The components of the doublets

Table 9. Characteristic frequencies of the stretching vibrations of PCl bonds in the spectra of several organophosphorus compounds.

Molecule	Assignment	Raman	IR
CH ₃ PCl ₂	$\nu_s(\text{PCl}_2)$, $\delta(\text{PCl}_2)$	483, vs, p (l)	479, vs (cr)
	$\nu_{as}(\text{PCl}_2)$, $t(\text{PCl}_2)$	483, vs, p (l)	479, vs (cr)
C ₂ H ₅ PCl ₂	$\nu_s(\text{PCl}_2)$, $\delta(\text{CCP})$	499, vs, p (g)	506, vs (g)
	$\nu_{as}(\text{PCl}_2)$	478, s, p (g)	498, vs (g)
n-C ₃ H ₇ PCl ₂	$\nu_s(\text{PCl}_2)$, $\nu_{as}[\text{PCl}_2(Gt)]$		512, vs (g)
	$\nu_s[\text{PCl}_2(Tt)]$	497, vs, p (l)	498, vs (g)
ClCH ₂ PCl ₂	$\nu_{as}(\text{PCl}_2)$	479, s, p (l)	482, s, sh (g)
	$\nu_{as}(\text{PCl}_2)$, $\nu_s[\text{PCl}_2(G)]$	494, vs (l)	508, vs (g)
CF ₃ PCl ₂	$\nu_s(\text{PCl}_2)$, $\nu_{as}[\text{PCl}_2(G)]$	494, vs, p (l)	498, vs (g)
	$\nu_{as}(\text{PCl}_2)$, $\delta_{as}(\text{CF}_3)$	523, w, dp (l)	526, vs (g)
(CH ₃) ₂ PCl	$\nu_s(\text{PCl}_2)$, $\delta_{as}(\text{CF}_3)$	516, vs, p (l)	520, vs (g)
	$\nu(\text{PCl})$, $w(\text{PC}_2)$	462, s, p (l)	533, vw, sh (cr)
	$w(\text{PC}_2)$, $\nu(\text{PCl})$	301, w, p (l)	460, s (cr)
			306, m (cr)

correspond to the in-phase and antiphase molecular vibrations in the dimers. Normal coordinate analysis for the molecule **17**⁵⁷ was based on the known experimental data,⁶⁷ which are somewhat different from those reported earlier.⁴⁹

Since vibrational spectra of CF₃PH₂ (**18**) and its deuterium-substituted analogue revealed no reduction of the C_{3v} local symmetry of the CF₃ group due to the addition of the PH₂ group, a normal coordinate analysis for this molecule was performed assuming this symmetry. An interpretation of the vibrational spectra of molecule **18**, based on the results obtained by Bürger *et al.*,⁶⁸ is given in Table 10; however, the description of the vibrations of the PH₂ fragment is somewhat changed to accord with the true C_s symmetry of the entire molecule.

Table 10. Interpretation of vibrational spectra of (trifluoromethyl)phosphine.

No.	Symmetry	Assignment	Raman (g)	IR (g)
10	A''	$\nu_{\text{as}}(\text{PH}_2)$		2348, vs
1	A'	$\nu_{\text{s}}(\text{PH}_2)$		2305, vs
2	A'	$\nu_{\text{as}}(\text{CF}_3)$, $\delta_{\text{as}}(\text{CF}_3)$	1184, w	1187, vs
11	A''	$\nu_{\text{as}}(\text{CF}_3)$, $\delta_{\text{as}}(\text{CF}_3)$	1184, w	1187, vs
3	A'	$\nu_{\text{s}}(\text{CF}_3)$, $\delta_{\text{s}}(\text{CF}_3)$, $\nu(\text{P}-\text{C})$	1140, w	1154, vs
4	A'	$\delta(\text{PH}_2)$	1072, w	1072, s
12	A''	$\tau(\text{PH}_2)$	848, m	833, vs
5	A'	$\omega(\text{PH}_2)$		833, vs
6	A'	$\delta_{\text{s}}(\text{CF}_3)$, $\nu_{\text{s}}(\text{CF}_3)$, $\nu(\text{P}-\text{C})$	745, s	743, m
7	A'	$\delta_{\text{as}}(\text{CF}_3)$	524, w	525, m
13	A''	$\delta_{\text{as}}(\text{CF}_3)$	524, w	525, m
8	A'	$\nu(\text{P}-\text{C})$, $\delta_{\text{s}}(\text{CF}_3)$	422, vs	419, s
9	A'	$r(\text{CF}_3)$	290, w	284, w
14	A''	$r(\text{CF}_3)$	290, w	284, w

Spectra of (CF₃)₂PH (**19**) and its deuterio analogue, as well as those of (CF₃)₃P (**20**) have been interpreted on the basis of normal coordinate analysis.^{69,70} Vibrational spectra^{54,71} of compounds CF₃PF₂ (**21**), CF₃PCl₂ (**22**), CF₃PBr₂ (**23**) and CF₃PI₂ (**24**) have been analysed.⁷²

Unlike vibrational spectra of unsubstituted alkylphosphines, those of alkyl(halogeno)phosphines are strongly dependent on the state of aggregation of the substances (see Tables 1–10). This can be rationalised by self-association of the molecules. Since routine spectral experiments usually do not include strong heating or cooling of specimens, the spectral indications of particular vibrations presented below are given for those states of aggregation, in which the compounds under study exist at ambient temperature.

Compared to unsubstituted compounds, spectral regions corresponding to vibrations of structural fragments constituting the molecules of alkyl(halogeno)phosphines become much wider. This is due to not only intermolecular interactions, but also relatively strong coupling of vibrations and strong substituents effects. Mention has been made¹ that the IR spectra of compounds of the type RPF₂ reveal two strong bands in the frequency ranges 806–869 and 860–947 cm⁻¹, which correspond to the vibrations $\nu_{\text{as}}(\text{PF}_2)$ and the $\nu_{\text{s}}(\text{PF}_2)$, respectively (see Table 6). As can be seen in Table 6, only the frequencies in the spectra of molecule **21** fall within the above-mentioned limits. Probably, a tendency of compounds containing the PF₂ group to undergo an autocatalytic disproportionation^{73,74} can be a reason for violation of the known correlations.¹ Analysis of the IR spectra of alkyl(difluoro)phosphines showed that both stretching vibrations of the PF₂ group are observed in the same characteristic region ~ 780–830 cm⁻¹. When assigning the vibrations, one should take into account that the $\nu(\text{PF}_2)$ frequencies can increase substantially on going from the liquid to vapour phase. In addition, our experience suggests that in the Raman spectra the $\nu_{\text{s}}(\text{PF}_2)$ lines are of medium or weak intensity and are polarised, while the $\nu_{\text{as}}(\text{PF}_2)$ lines are weak and depolarised (though quantitative

differences between the degrees of depolarisation of these lines can be rather small). Introduction of halogen atoms into molecules causes an increase in the force constants of the P–F bonds, so that the $\nu(\text{PF}_2)$ frequencies can be as high as 870 cm⁻¹.

The frequencies of stretching vibrations of the PCl₂ groups lie in the region 420–526 cm⁻¹ (see the monograph¹). For alkyl(halogeno)phosphines, they are usually close to the upper bound of this spectral region (~ 450–526 cm⁻¹). The frequencies of the vibrations $\nu_{\text{s}}(\text{PCl}_2)$ of alkyl(dichloro)phosphines are somewhat higher than those of the vibrations $\nu_{\text{as}}(\text{PCl}_2)$ [the opposite is observed for molecules **16** and **22** (see Table 9)]; in the spectra of liquids the corresponding peaks usually coalesce into an unresolved contour. These compounds are characterised by an increase in the frequencies of stretching vibrations of the PCl₂ group on going to the gas phase. However, both the IR spectral bands and the Raman lines remain very strong, which facilitates the identification of these $\nu(\text{PCl}_2)$ vibration in spite of their strong coupling with other vibrations (see Table 9).

The vibrations $\nu(\text{P}-\text{Cl})$ of the molecule **17** are strongly mixed with the rocking vibrations of the (CH₃)₂P group, which gives rise to two co-operative vibrations. Among them, the vibration with the higher frequency can be rather arbitrarily associated with the $\nu(\text{P}-\text{Cl})$ stretch (see Table 9). Analysis of scarce spectral data for dialkyl(chloro)phosphines suggests that the frequencies of the vibrations $\nu(\text{P}-\text{Cl})$ of these compounds lie in nearly the same spectral region as those of the vibrations $\nu(\text{PCl}_2)$ (see above). Therefore, the most pronounced distinction between the corresponding spectra is reduced to the appearance of two vibrations, *viz.*, $\nu_{\text{s}}(\text{PCl}_2)$ and $\nu_{\text{as}}(\text{PCl}_2)$, in the spectra of dialkyl(chloro)phosphines instead of one $\nu(\text{P}-\text{C})$ vibration in the spectra of alkyl(dichloro)phosphines. The frequencies of the vibrations $\nu(\text{PCl}_2)$ and $\nu(\text{P}-\text{C})$ in the spectra of alkyl(halogeno)phosphines (see Table 5) are observed near the upper bounds of the corresponding spectral regions (see Section II) for alkylphosphines. (The molecules containing the CH₂Cl and CF₃P groups are exceptions to this rule. Their spectra are discussed below.) The intensities of the corresponding bands in the IR spectra of alkyl(halogeno)phosphines are usually higher than those in the spectra of unsubstituted analogues. Other parameters of these spectral peaks are similar to those discussed above (see Section II).

Spectral indications of the CH₃P and C₂H₅P groups are nearly identical for alkylphosphines and their halogeno-substituted derivatives. The exceptions are the vibrations with predominant contribution of the $r(\text{CH}_3\text{P})$ vibration, since their frequencies decrease from ~ 940–985 down to ~ 880 cm⁻¹ upon introduction of halogen atoms to the phosphorus atom in the last-named molecules. The intensities of the corresponding bands in the IR spectra are rather high.

The peaks in the region 1380–1410 cm⁻¹, corresponding to the $\delta(\text{CH}_2)$ vibrations, are characteristic of the CH₂Cl group. (This spectral region is characteristic of the vibrations of CH₂X groups, where X is a rather heavy atom; *e.g.*, X = P or S). Stretching vibrations of the C–Cl bond of the CH₂Cl group strongly interact with the vibrations $\nu(\text{P}-\text{C})$ and give rise to two new vibrations. Among them, the vibration with the lower frequency is observed in the region typical of the vibration $\nu(\text{P}-\text{C})$ and has all the specific spectral indications (see Section II). The peaks corresponding to the second stretching vibration of the PCCl group are observed in the region ~ 740–790 cm⁻¹ and have variable intensities.

The vibrations of the CF₃P group are readily identified in the spectra of any organophosphorus compounds. Mention has been made⁴ that very strong IR absorption bands in the region 1100–1300 cm⁻¹ correspond to the stretching vibrations of trifluoromethyl groups. For phosphines, this correlation has specific details.

Two very strong bands in the region 1140–1235 cm⁻¹ of the IR spectra of phosphines can be arbitrarily assigned to the vibrations $\nu_{\text{as}}(\text{CF}_3)$ (Table 11), which result from the mixing of the stretching and deformation [$\delta_{\text{as}}(\text{CF}_3)$] vibrations. They are

Table 11. Vibration $\nu_{\text{as}}(\text{CF}_3)$ in the spectra of organophosphorus compounds.

Molecule	Assignment	Raman	IR
CF_3PH_2	$\nu_{\text{as}}(\text{CF}_3), \delta_{\text{as}}(\text{CF}_3) (\parallel)$	1184, w (g)	1187, vs (g)
	$\nu_{\text{as}}(\text{CF}_3), \delta_{\text{as}}(\text{CF}_3) (\perp)$	1184, w (g)	1187, vs (g)
CF_3PI_2	$\nu_{\text{as}}(\text{CF}_3), \delta_{\text{as}}(\text{CF}_3) (\parallel)$		1177, vs (g)
	$\nu_{\text{as}}(\text{CF}_3), \delta_{\text{as}}(\text{CF}_3) (\perp)$		1140, vs (g)
CF_3PBr_2	$\nu_{\text{as}}(\text{CF}_3), \delta_{\text{as}}(\text{CF}_3) (\parallel)$	1184, m (l)	1190, vs (g)
	$\nu_{\text{as}}(\text{CF}_3), \delta_{\text{as}}(\text{CF}_3) (\perp)$	1156, sh (l)	1160, sh (g)
CF_3PCl_2	$\nu_{\text{as}}(\text{CF}_3), \delta_{\text{as}}(\text{CF}_3) (\parallel)$	1200, w (l)	1200, vs (g)
	$\nu_{\text{as}}(\text{CF}_3), \delta_{\text{as}}(\text{CF}_3) (\perp)$	1184, m (l)	1176, m (g)
CF_3PF_2	$\nu_{\text{as}}(\text{CF}_3), \delta_{\text{as}}(\text{CF}_3) (\parallel)$	1222, m (g)	1222, vs (g)
	$\nu_{\text{as}}(\text{CF}_3), \delta_{\text{as}}(\text{CF}_3) (\perp)$	1166, m (g)	1170, sh (g)
$(\text{CF}_3)_2\text{PH}$	$\nu_{\text{as}}(\text{CF}_3), \delta_{\text{as}}(\text{CF}_3)$		1212, vs (g)
	$\nu_{\text{as}}(\text{CF}_3), \nu(\text{CF}_3)$		1180, vs (g)
$(\text{CF}_3)_3\text{P}$	$\nu_{\text{as}}(\text{CF}_3), \delta_{\text{as}}(\text{CF}_3) (\parallel)$		1235, s (g)
	$\nu_{\text{as}}(\text{CF}_3), \delta_{\text{as}}(\text{CF}_3) (\perp)$	1176, w, br (g)	1189, s (g)

Note. Hereafter ($\parallel$) and ($\perp$) respectively denote the vibrations, which occur parallel and perpendicular to the molecular symmetry plane.

localised within one CF_3P group and do not interact kinematically with the motions of adjacent fragments. Therefore, variations of the frequencies of the vibrations $\nu_{\text{as}}(\text{CF}_3)$ are due to dynamic reasons alone and, hence, reflect the changes in the electronic structure of the phosphorus-containing fragment of the molecule. The $\nu_{\text{as}}(\text{CF}_3)$ frequencies increase as the electronegativities of substituents at the phosphorus atom increase (see Table 11).

Symmetrical stretching vibrations $\nu_s(\text{CF}_3)$ mix with the bending vibrations $\delta_s(\text{CF}_3)$ and the vibrations $\nu(\text{P}-\text{C})$ (see Table 10). The involvement of the phosphorus atom in the vibrations provides the possibility for kinematic interactions between adjacent groups to occur, which is particularly effective in the case of equal 'individual' frequencies. That is why the number of bands corresponding to the vibration $\nu_s(\text{CF}_3)$ in the IR spectra of compounds with one CF_3P group and with two (or three) CF_3P groups is different, namely, one very strong band in the region $1100-1160\text{ cm}^{-1}$ vs. two bands in the same spectral region, respectively.

Previously (see Section II), particular attention was paid to the vibrations $\nu(\text{P}-\text{C})$ and it was shown that the corresponding Raman lines have distinctive spectral indications, which are common to various organophosphorus compounds with the $\text{P}-\text{C}(\text{sp}^3)$ valence bonds. Unfortunately, compounds with the CF_3P group are exceptions to this rule, since all attempts to discriminate between the vibrations with predominant contribution of the $\text{P}-\text{C}$ bond and other normal coordinates have failed. The vibrations denoted ⁴ as $\nu(\text{P}-\text{C})$ are in fact coupled vibrations with nearly equal contributions of the vibrations $\delta_s(\text{CF}_3)$ and $\nu_s(\text{CF}_3)$ and with a some contributions of the vibrations $\nu(\text{P}-\text{C})$ (see Table 10). The corresponding bands in the vibrational spectra of organophosphorus compounds are observed in the region between 650 and 750 cm^{-1} . For phosphines, this region is much narrower, namely, one or two strong IR absorption bands are observed in the frequency range $\sim 720-750\text{ cm}^{-1}$. The corresponding Raman lines are polarised and intense.

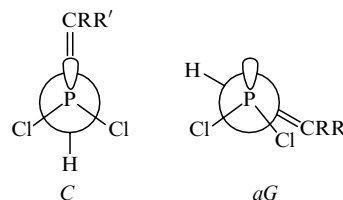
Vibrations of the $\text{P}-\text{C}$ bonds make somewhat greater contributions to the coupled vibrations denoted ⁴ as $\delta(\text{C}-\text{F})$. The corresponding IR absorption bands and Raman lines ($\sim 410-470\text{ cm}^{-1}$) are rather strong, the latter being polarised, which facilitates vibrational assignments.

We suggest that the Raman lines of medium or weak intensity, which are observed in the region $520-570\text{ cm}^{-1}$ and correspond to the vibrations with the predominant contribution of the vibrations $\delta_{\text{as}}(\text{CF}_3)$, can also be used for identification of compounds under consideration. The intensities of the $\delta_{\text{as}}(\text{CF}_3)$ bands in the IR spectrum can vary from very weak to strong.

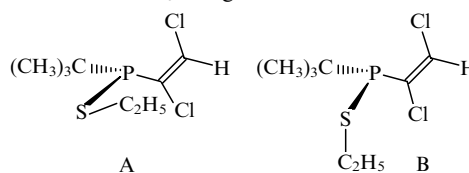
IV. Phosphines with unsaturated groups at the phosphorus atom

To date, a normal coordinate analysis has been performed only for three groups of the trivalent phosphorus compounds with unsaturated fragments. These are the molecules with the $\text{P}-\text{C}=\text{C}$ fragment, ethynylphosphines and cyano derivatives of phosphines.

The first group comprises alkenyl(dichloro)phosphines. Their molecules can adopt both the *cis* (*C*) and *anti,gauche* (*aG*) conformations.



According to the vibrational spectroscopy data,⁷⁵ the *cis* conformers of the molecules $\text{CH}_2=\text{CHPCl}_2$ (**25**) and $(\text{CH}_3)_2\text{C}=\text{CHPCl}_2$ (**26**) are dominant in the condensed phase, whereas liquid dichloro(styryl)phosphine (**27**) is a mixture of both conformers. Because of steric hindrances, in the molecule of *S*-ethyl *tert*-butyl(1,2-dichlorovinyl)phosphinothioite (**28**) the $\text{C}=\text{C}$ bond is in *cis* position with respect to the lone electron pair (LEP) of the phosphorus atom.⁷⁶ However, it is believed that a mixture of conformers can exist in the liquid owing to internal rotation of the $\text{C}_2\text{H}_5\text{S}$ fragment



The interpreted vibrational spectra⁷⁵ of the simplest representative of this group of compounds, *viz.*, compound **25**, are listed in Table 12.

Triethynylphosphine (**29**) is a representative of the second group of the trivalent phosphorus compounds with unsaturated fragments. Its molecule has a C_{3v} symmetry and the vibrations of the A_2 type are optically inactive and not observed in vibrational spectra. Table 13 lists the experimental⁷⁷ vibrational spectra of compound **29** and the assignments⁷⁸ based on the results of normal coordinate analysis. Unfortunately, neither the eigenvectors of the vibrations nor the potential energy distribution over the

Table 12. Interpretation of vibrational spectra of dichloro(vinyl)phosphine.

No.	Symmetry	Assignment	Raman (l)	IR (l)
4	A'	$\nu(\text{C}=\text{C}), \delta(\text{CH}_2), \delta(\text{PCH})$	1605, sh, w, 0.20	1592, vw
		$\nu(\text{P}-\text{C})$	1595, m, 0.17	
5	A'	$\delta(\text{CH}_2), \nu(\text{C}=\text{C})$	1392, m, 0.22	1391, m
6	A'	$\delta(\text{PCH}), \nu(\text{CH}_2), \delta(\text{CH}_2)$	1255, m, 0.21	1255, w
13	A''	$\gamma(\text{CH}_2)$	1028, vw	1037, vw
7	A'	$\nu(\text{CH}_2), \nu(\text{P}-\text{C})$	1010, w	1011, m
14	A''	$\chi(\text{C}=\text{C}), \gamma(\text{CH}_2), \gamma(\text{PCH})$	971, w	965/976, w
8	A'	$\nu(\text{PC}), \nu(\text{CH}_2)$	720, m, 0.42	719, s
15	A''	$\gamma(\text{PCH}), \nu(\text{PCl}_2)$	587, w, 0.74	585, s
9	A'	$\nu_s(\text{PCl}_2), \delta(\text{PCl}_2)$	502, vs, 0.25	504, vs
16	A''	$\nu_{\text{as}}(\text{PCl}_2)$	473, s, 0.42	473, vs
10	A'	$\nu(\text{C}=\text{C})$	348, vs, 0.15	347, w
11	A'	$\delta(\text{PCl}_2)$	255, m, 0.50	258, m
17	A''	$\nu(\text{PCl}_2), \gamma(\text{PCH})$	218, m, 0.86	218, m
12	A'	$\nu(\text{PCl}_2)$	190, s, 0.83	188, m

Table 13. Interpretation of vibrational spectra of triethynylphosphine.

No.	Symmetry	Assignment	Raman (s) ^a	IR (s) ^b
2	A ₁	$\nu(\text{C}\equiv\text{C})$	2054, 100, p	2053, m
10	E	$\delta(\text{C}\equiv\text{C})$	2054, 100, p	2053, m
3	A ₁	$\delta(\text{C}\equiv\text{CH}) (\parallel)$	702, 2	696, vs
11	E	$\delta(\text{C}\equiv\text{CH}) (\parallel)$	702, 2	696, vs
12	E	$\delta(\text{C}\equiv\text{CH}) (\perp)$	654, 1	651, s, sh
13	E	$\nu_{\text{as}}(\text{PC}_3)$	643, 3	639, vs
4	A ₁	$\nu_{\text{s}}(\text{PC}_3)$		614, w
5	A ₁	$\delta(\text{PC}\equiv\text{C}) (\parallel)$	449, 2	444, m
14	E	$\delta(\text{PC}\equiv\text{C}) (\parallel)$		423, m
15	E	$\delta(\text{PC}\equiv\text{C}) (\perp)$	273, 4	270, m
6	A ₁	$\delta_{\text{s}}(\text{PC}_3)$		131, m, v.br
16	E	$\delta_{\text{as}}(\text{PC}_3)$	106, 71, dp	100.5, vw ^c

^a The frequencies were averaged over the spectra of solutions in CCl₄ and furan. ^b The frequencies were averaged over the spectra of solutions in CCl₄ and CS₂. ^c From the gas-phase spectrum.

vibrational coordinates have been reported,⁷⁸ therefore the assignments listed in Table 13 seem to be tentative.

Vibrational spectra of dicyano(methyl)phosphine (**30**)⁷⁹ and tricyanophosphine (**31**)^{80–82} have been studied. The spectra reported by Goubeau, Haeberle and Ulmer⁸⁰ differ appreciably from those reported in the other studies.^{81,82} This is probably due to chemical transformations of the substances during the preparation of the samples.⁸² In the condensed phase, both compounds can be involved in strong intermolecular interactions, which can cause rather large shifts of the spectral peaks (Table 14) and even be responsible for the appearance of new bands as compared to the gas-phase spectra. For instance, an intense peak at $\sim 630\text{ cm}^{-1}$ (see Refs 79, 81, 82) in the spectra of liquid and crystalline cyanophosphines and their solutions in CH₃CN is not observed in the spectra of vapours or solutions in other solvents. This peak results from intermolecular interactions involving the cyano groups.^{79,82} Such strong effects hamper the interpretation of the spectra of these molecules in the liquid or crystalline phase. It should be noted that the molecule **31** has a C_{3v} symmetry and vibrations belonging to the A₂ type are optically inactive and not observed in vibrational spectra. The force field of the molecule **31** has been first evaluated by Unnikrishnan and Aruldas.⁸³ How-

Table 14. Interpretation of vibrational spectra of phosphorus tricyanide.

No.	Symmetry	Assignment	Raman (g)	Raman (s) ^a	Raman (cr)	IR (cr)
1	A ₁	$\nu(\text{C}\equiv\text{N})$	2197, s, p	2196, s, p	{ 2210, w 2205, w	
6	E	$\nu(\text{C}\equiv\text{N})$		2190, vw		2201.2, s
2	A ₁	$\nu_{\text{s}}(\text{PC}_3)$, $\delta(\text{PCN}) (\perp)$, $\delta_{\text{s}}(\text{PC}_3)$	625, w, p	606, s, p	604, s	603, s
7	E	$\nu_{\text{as}}(\text{PC}_3)$		581, w, dp	577, w	
3	A ₁	$\delta(\text{PCN}) (\perp)$, $\nu_{\text{s}}(\text{PC}_3)$	451, w, p	464, w, dp	469, m	468, w
8	E	$\delta(\text{PCN}) (\perp)$, $\delta_{\text{as}}(\text{PC}_3)$	442, vw	452, w, p	453, w	452, w
9	E	$\delta(\text{PCN}) (\parallel)$, $\delta_{\text{as}}(\text{PC}_3)$		312, w, dp	318, w	314, w
4	A ₁	$\delta_{\text{s}}(\text{PC}_3)$, $\delta(\text{PCN}) (\perp)$	128, m, dp		(148, w)	(145, w)
10	E	$\delta_{\text{as}}(\text{PC}_3)$, $\delta(\text{PCN}) (\parallel)$	105, s, dp	(130, m, dp)	(112, vw)	

Note. The frequencies assigned tentatively are given in parentheses.

^a A solution in CH₃CN.

ever, calculations performed using this force field have led to unrealistic values of the root-mean-square vibrational amplitudes.⁸⁴ Therefore, Table 14 lists the theoretical interpretation of the spectra of compound **31** according to other studies.^{84,85} The results of normal coordinate analysis for the spectra of dicyano(methyl)phosphine **30** have been reported.⁸⁶

A common feature of the spectra of the three groups of compounds considered in this Section is that the frequencies of stretching vibrations of the multiple bonds at the trivalent phosphorus atom are lower than those for the corresponding organic molecules. For instance, the frequencies of stretching vibrations of the C=C(P) group (see Table 12) are lower than the lower bound of the spectral region 1620–1680 cm^{−1} typical of alkenes.⁸⁷ As is known, the introduction of halogens also leads to a decrease in the frequency of the stretching vibrations $\nu(\text{C}=\text{C})$; however, this effect is not so strong as that observed after introduction of the phosphorus atom. For instance, the frequency of the vibrations $\nu(\text{C}=\text{C})$ in CCl₂=CHCl is 1589 cm^{−1} (cf. 1539 cm^{−1} for the molecule **28**). The same is also observed for the frequency of the vibrations $\nu(\text{C}\equiv\text{C})$ in compound **29** (see Table 13), which is lower than the corresponding frequencies in acetylene and haloacetylenes ($\sim 2085\text{--}2270\text{ cm}^{-1}$).^{87,88} The frequencies of the stretching vibrations $\nu(\text{C}\equiv\text{N})$ of molecules **30** and **31** also lie far below the spectral region 2215–2260 cm^{−1} typical of organic cyanides.⁸⁷ It should be noted that the peaks at $\sim 2180\text{--}2217\text{ cm}^{-1}$ are ‘fingerprint’ of the PCN groups in the spectra of neat liquids or crystals (see monograph¹). A small overlap of the two spectral regions^{1,87} is of no concern for trivalent phosphorus compounds, since the corresponding frequencies of stretching vibrations of the PCN group always lie below 2215 cm^{−1}. At the same time, it should be remembered that the $\nu(\text{C}\equiv\text{N})$ frequencies of halonitriles⁸⁹ lie nearly in the same region as the $\nu(\text{PCN})$ frequencies. The $\nu(\text{C}=\text{C})$, $\nu(\text{C}\equiv\text{C})$ and $\nu(\text{C}\equiv\text{N})$ bands in the IR spectra can be of weak intensity, therefore it is more convenient to identify these groups using the Raman spectra in which the corresponding lines always are sufficiently strong and polarised.

Raman spectroscopy can also be used to assign the vibrations denoted⁸⁷ as $\delta(\text{CH}_2)$ and $\delta(\text{C}-\text{H})$, since the lines associated with them are polarised and are of medium intensity. The frequency of the vibration $\delta(\text{CH}_2)$ of the vinyl radical at the phosphorus atom is observed in the region 1390–1410 cm^{−1} (cf. 1410–1420 cm^{−1} in the spectra of terminal alkenes). The frequencies of the vibrations $\delta(\text{C}-\text{H})$ of monosubstituted styrenes⁸⁷ lie in the region 1295–1310 cm^{−1} [cf. 1335 cm^{−1} for dichloro(styryl)phosphine **27**]. The $\delta(\text{C}-\text{H})$ vibrations in the molecules of terminal alkenes are observed in the spectral region 1290–1300 cm^{−1} (see Ref. 87), while the frequency of the vibration $\delta(\text{PCH})$ of the vinyl group at the phosphorus atom varies between 1250 and 1260 cm^{−1} (see Table 12). The $\gamma(\text{CH}_2)$ and $\chi(\text{C}=\text{C})$ frequencies also ‘drop out’ of the corresponding spectral regions typical of alkenes.⁸⁷ Changes in the ‘fingerprint’ vibrational frequencies of alkenylphosphines as compared to those of alkenes are due to the effect of the phosphorus atom on the force constants of the alkenyl fragment rather than kinematic effects.

V. Alkoxy derivatives of trivalent phosphorus

The spectra of both cyclic and acyclic alkoxy derivatives of trivalent phosphorus have been studied. According to *ab initio* calculations,^{90–92} the simplest acyclic molecules such as methyl dimethylphosphinite (**32**), methyl phosphorodifluoridite (**33**) and methyl phosphorodichloridite (**3**) can adopt both the *T* and *G* conformations (see Fig. 1; X = CH₃, F, Cl; Y = O; Z = CH₃). Studies of the vibrational spectra of molecule **32** and its isotopomers CD₃OP(CH₃)₂, CH₃OP(CD₃)₂ and CD₃OP(CD₃)₂ showed that both conformers were present in the liquid and gas states,⁹³ while only the *trans* conformer was retained in crystals. It should be noted that the interpretation of incomplete spectra of methyl dimethylphosphinite **32** (see Seel and Velleman⁹⁴) is in agreement

Table 15. Interpretation of vibrational spectra of methyl phosphorodichloridite.

No.	Symmetry	Assignment	Raman (l)	IR (g)
5	A'	$r(\text{CH}_3)$, $\nu_{\text{as}}(\text{POC})$	1181, 15, p	1181, s
14	A''	$r(\text{CH}_3)$	1154, 50, dp	1151, m ^a
6	A'	$\nu_{\text{as}}(\text{POC})$, $r(\text{CH}_3)$	1044, 50, p	1057, vs
7	A'	$\nu_{\text{s}}(\text{PF}_2)$	816, 100, p	829, vs
15	A''	$\nu_{\text{as}}(\text{PF}_2)$	778, 5, dp	797, vs
8	A'	$\nu_{\text{s}}(\text{POC})$	778, 39, p	784, m
9	A'	$r(\text{PF}_2)$, $\delta(\text{POC})$, $\delta(\text{PF}_2)$	536, 40, p	539, m
16	A''	$t(\text{PF}_2)$, $\chi(\text{PO})$	370, 20, p	370, s
10	A'	$\delta(\text{PF}_2)$	351, 10, p	358, sh
11	A'	$\delta(\text{POC})$, $r(\text{PF}_2)$	218, 30, p	214, s
17	A'	$\chi(\text{PO})$, $\chi(\text{O}-\text{CH}_3)$, $t(\text{PF}_2)$	128, 10, dp	120, m
18	A''	$\chi(\text{O}-\text{CH}_3)$, $\chi(\text{PO})$	81, 14, dp	

^a From the spectrum of crystals.

with the assignments suggested on the basis of *ab initio* quantum-chemical calculations.^{90,93}

Both vibrational^{91,95} and microwave⁹⁶ spectral studies as well as a gas-phase electron diffraction study⁹⁷ revealed no indications of the *gauche* conformers of the molecule of methyl phosphorodichloridite **33**. Therefore, the interpretation of the IR absorption bands and Raman lines in the spectra of compound **33** (Table 15) is based on the results of *ab initio* calculations of the vibrations of the *trans* conformer.⁹¹

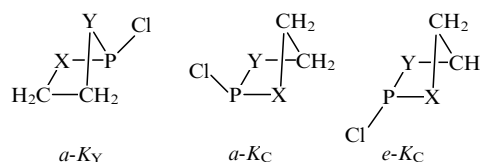
Data on rotational isomerism in the molecule of methyl phosphorodichloridite **3** are contradictory.^{92,98–103} In spite of this, the existence of *trans* conformers of molecule **3** is doubtless,^{92,102,103} and the interpretation of the spectra of *trans* conformer was based on the results of *ab initio* calculations of the vibrations.⁹²

The molecule of ethyl phosphorodichloridite (**34**) can adopt five stable conformations¹⁰⁴ (see Fig. 2; X = Cl, Y = O); however, this has not been confirmed experimentally. Using normal coordinate analysis, it has been shown¹⁰⁴ that the observed spectra can be attributed to the *Tt* and/or *Gt* conformers. The interpretation of the spectra (see Table 16) is based on the results of normal coordinate analysis for the *Tt* conformer.²⁶

The molecule of β -thiocyanatoethyl phosphorodichloridite (**35**) can adopt twenty-three stable conformations. In the liquid state, compound **35** exists as a mixture of at least three conformers, while in the crystalline state (at low temperatures) the

number of conformers equals at least two.¹⁰⁵ Since conformational analysis of compound **35** is too complicated, attempts to determine unambiguously the number and type of observable conformers of molecule **35** have failed. It has only been shown¹⁰⁵ that the mutual *gauche*-orientation of the O–C and C–S bonds is energetically favourable. The interpretation of the IR absorption bands and Raman lines in the spectra of β -thiocyanatoethyl phosphorodichloridite **35** is based on the results of normal coordinate analysis for all possible conformers.¹⁰⁵

A few studies devoted to the normal coordinate analysis of cyclic alkoxy derivatives of trivalent phosphorus has been reported. Five-, six- and seven-membered phosphacycles with the P–O–C fragment have been studied. First, consider the spectra and conformations of five-membered organophosphorus compounds. According to the vibrational spectroscopy data,¹⁰⁶ the molecule of 2-chloro-1,3,2-dioxaphospholane (**36**) adopts a single conformation. Gas-phase electron diffraction study¹⁰⁷ of compound **36** revealed a stable (in the gas phase) conformation of molecule **36** shown in Fig. 3 (*a-E_O*, X = Y = O). Earlier, a normal coordinate analysis for 2-chloro-1,3,2-dioxaphospholane **36** has been performed for a symmetrical 'envelope' conformation in which the phosphorus atom deviates from the plane passing through the other ring atoms¹⁰⁶ (*a-E_P*). Next to the publication cited,¹⁰⁷ a normal coordinate analysis for the non-symmetrical *a-E_O* conformer (see Fig. 3) has been reported.¹⁰⁸ It is this version of the interpretation of the spectra that is listed in Table 17.

**Figure 3.** The 'envelope' conformations of the molecules of 2-chloro-1,3,2-dioxathia(phospholane)s: with apical Y atom and pseudoaxial orientation of the P–Cl bond (*a-E_Y*), with apical C atom and axial orientation of the P–Cl bond (*a-E_C*) and with apical C atom and equatorial orientation of the P–Cl bond (*e-E_C*).

2-Chloro-1,3,2-oxathiaphospholane (**37**) exists in the liquid state and in solutions as a mixture of two non-symmetrical conformers shown in Fig. 3 (*a-E_C* and *e-E_C*; X = O, Y = S).^{108,109} Their vibrational spectra^{108,109} have been interpreted theoretically.¹⁰⁸

The molecule of 2-chloro-1,3,2-dioxaphosphorinane (**38**) adopts a single conformation.¹¹⁰ Based on the results of the gas-phase electron diffraction study,¹¹¹ the conformation *a* was suggested for its molecule; at the same time, the band-shape

Table 16. Interpretation of vibrational spectra of ethyl phosphorodichloridite.

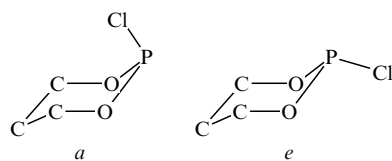
No.	Symmetry	Assignment	Raman (l)	IR (l) ^a
8	A'	$\nu(\text{OC})$, $\nu(\text{CC})$, $\delta(\text{POC})$, $\delta(\text{OCC})$	1095, vw, 0.4	1095, vw
9	A'	$\nu_{\text{as}}(\text{POC})$, $\nu(\text{CC})$, $w(\text{CH}_2)$	1022, vw	1022, vs
10	A'	$\nu(\text{CC})$, $\nu(\text{PO})$, $w(\text{CH}_3)$		963, s
22	A''	$r(\text{CH}_2)$, $r(\text{CH}_3)$	727, m, 0.6	735, m
11	A'	$\nu_{\text{s}}(\text{POC})$, $\nu(\text{CC})$, $\delta(\text{POC})$, $w(\text{CH}_2)$	727, m, 0.6	735, m
12	A'	$\nu_{\text{s}}(\text{PCl}_2)$	493, vs, 0.3	500, s
23	A''	$\nu_{\text{as}}(\text{PCl}_2)$	443, m, dp	450, s
13	A'	$\delta(\text{POC})$, $\delta(\text{OCC})$, $w(\text{PCl}_2)$	422, m, 0.8	430, sh
14	A'	$\delta(\text{OCC})$, $\delta(\text{POC})$, $w(\text{PCl}_2)$	300, vw	
24	A''	$t(\text{PCl}_2)$, $\chi(\text{PO})$, $\chi(\text{OC})$	300, vw	
15	A'	$\delta(\text{PCl}_2)$	192, s, 0.6	
25	A''	$t(\text{PCl}_2)$, $\chi(\text{CC})$	150, w, 0.67	
16	A'	$\delta(\text{POC})$, $\omega(\text{PCl}_2)$, $\delta(\text{PCl}_2)$	125, vw, dp	

^a Spectral region below 400 cm^{−1} has not been recorded.**Table 17.** Interpretation of vibrational spectra of 2-chloro-1,3,2-dioxaphospholane.

No.	Assignment	Raman (l)	IR (l) ^a
11	$\nu_{\text{as}}(\text{POC})$		1048, sh
12	$\nu_{\text{as}}(\text{CCO})$	1009, 20, p	1010, s
13	$r(\text{CH}_2)$		984, sh
14	$\nu(\text{CC})$, $\nu_{\text{as}}(\text{POC})$, $\delta(\text{CCO})$	922, 20, p	928, s
15	$\nu_{\text{s}}(\text{POC})$, $\nu_{\text{as}}(\text{POC})$, $r_{\text{as}}(\text{CH}_2)$	805, 100, p	809, m
16	$\nu_{\text{as}}(\text{POC})$, $r(\text{CH}_2)$, $\delta(\text{POC})$	767, 5	764, s
17	$\nu(\text{PO})$, $r(\text{CH}_2)$	754, 5	750, sh
18	$\delta_{\text{as}}(\text{CCO})$, $\delta_{\text{as}}(\text{POC})$	602, 10, p	597, m
19	$\nu(\text{PCl})$	443, 70, p	445, s
20	$\delta(\text{OPO})$, $\delta_{\text{s}}(\text{POC})$	330, 60, p	
21	$\delta_{\text{as}}(\text{OPCl})$	258, 10, p	

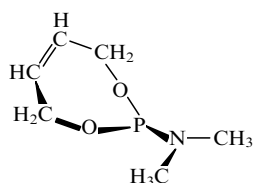
^a Spectral region below 400 cm^{−1} has not been recorded.

analysis of the IR spectra of compound **38** in the vapour phase counts in favour of conformation *e*.¹¹⁰



A normal coordinate analysis for both conformers of the molecule of 2-chloro-1,3,2-dioxaphosphorinane **38** has been performed.^{110, 112}

The molecule of 4,7-dihydro-2-dimethylamino-1,3,2-dioxaphosphin (**39**) adopts mainly a non-symmetrical conformation.¹¹³



for which theoretical interpretation of the vibrational spectra has been carried out.¹¹³

Based on the results of normal coordinate analyses (see Tables 15–17), it is possible to establish the origin of the bands used as spectral indications of the presence of different AlkOP groups in the molecules under study. It is known that the methoxy group at the phosphorus atom is responsible for the appearance of a strong band at $\sim 1010\text{--}1050\text{ cm}^{-1}$, a strong or medium band in the region $\sim 700\text{--}800\text{ cm}^{-1}$ and a medium or weak (often multiplet) band in the region $\sim 1150\text{--}1200\text{ cm}^{-1}$ in the IR spectra. The first two bands are associated with the antiphase and in-phase stretching vibrations of the P–O and O–C bonds, respectively. The former bond makes the major contribution to the symmetric vibration $\nu_s(\text{POC})$, while the latter contributes largely to the antisymmetric vibration $\nu_{as}(\text{POC})$. Mention may be made that the vibrations $\nu_s(\text{POC})$ can also be readily identified using the Raman spectra, since the corresponding line is of rather high intensity and polarised. Weak Raman lines and IR absorption bands in the spectral region $\sim 1150\text{--}1200\text{ cm}^{-1}$ are mainly due to the rocking vibrations of the methyl group.

Spectral ‘fingerprints’ of the $\text{C}_2\text{H}_5\text{OP}$ group are well known.^{1–5} These are the strong bands in the IR spectra in the regions $\sim 900\text{--}970$, $\sim 1010\text{--}1040\text{ cm}^{-1}$ and the bands of medium or weak intensity in the regions $\sim 1090\text{--}1110$ and $\sim 1150\text{--}1170\text{ cm}^{-1}$. All of them are due to strongly coupled vibrations (Table 16). The vibration with the highest frequency is associated with the rocking motion $\nu(\text{CH}_2)$. The frequencies of stretching vibrations of the OCC fragment usually lie in the range $\sim 1090\text{--}1110\text{ cm}^{-1}$. Strong bands in the IR spectrum are to a certain degree due to the antiphase stretching vibrations of the P–O, O–C and C–C bonds (see Table 16, stretching vibrations Nos 9 and 10). The vibration $\nu_s(\text{POC})$ gives rise to the appearance of rather intense spectral peaks both in the IR and Raman spectra (stretching vibration No. 11). They are observed in the region $\sim 700\text{--}800\text{ cm}^{-1}$, the corresponding Raman line being polarised.

This spectral region is characteristic of the frequencies of the vibrations $\nu_s(\text{POC})$ for not only the ethoxy group, but almost any alkoxy groups at the trivalent phosphorus atom. Only for cyclic alkoxy derivatives does the region extend to $\sim 690\text{--}820\text{ cm}^{-1}$. Because of the possibility that the molecules of compounds under study adopt several conformations owing to internal rotation about the P–O bond, the bands corresponding to the vibrations $\nu_s(\text{POC})$ can split into doublets. It should be noted that if a molecule contains two POC groups at the phosphorus atom, their stretching vibrations effectively interact through this atom (see Section I). For instance, the frequencies of the ring ‘breathing’

vibrations corresponding to the synchronous stretch or contraction of the bonds in both POC groups (see Table 17, vibrations No. 15) and to the antiphase vibrations of these fragments (vibrations No. 16) are observed in this region of the spectra of 2-chloro-1,3,2-dioxaphospholane. The IR absorption bands associated with the antiphase vibrations $\nu_s(\text{POC})$ are usually more intense than those corresponding to the in-phase vibrations. At the same time, the lines of the in-phase vibrations in the Raman spectra are symmetrical, very strong and strongly polarised, while those of the antiphase vibrations are, as a rule, of weak intensity.

It should be noted that the ring ‘breathing’ vibrational frequencies of 1,3,2-dioxaphospholanes are always higher than the frequencies of the in-phase vibrations $\nu_s(\text{POC})$ of related acyclic organophosphorus compounds, as well as those of the ring ‘breathing’ vibrations of 1,3,2-dioxaphosphorinanes¹¹² and other related unstrained phosphacyclanes (provided that the exocyclic groups in the dioxaphospholane and in the larger ring to be compared are the same). A remarkable feature of 1,3,2-dioxaphospholanes is that the frequencies of the ring ‘breathing’ vibrations are higher than those of the antiphase vibrations $\nu(\text{POC})$. The opposite is observed for 1,3,2-dioxaphosphorinanes and acyclic dialkoxy derivatives. These distinctions can be used for analytical purposes. If the molecules under study have exocyclic P–Cl bonds, then the strong IR absorption bands and very strong polarised Raman lines in the spectral region $\sim 440\text{--}460\text{ cm}^{-1}$ provide reliable spectral indications of the 1,3,2-dioxaphospholane rings. These spectral bands and lines are due to the stretching vibrations of the P–Cl bond. In the molecules of 1,3,2-dioxaphosphorinanes, the vibrations $\nu(\text{P–Cl})$ interact with the ring deformation vibrations. Two resultant vibrations appear in the spectra as the intense IR absorption bands and Raman lines in the regions $\sim 400\text{--}430$ and $\sim 460\text{--}490\text{ cm}^{-1}$. The most characteristic of the spectra of acyclic phosphorochloridites are intense IR absorption bands in the region $\sim 490\text{--}510\text{ cm}^{-1}$. Thus, the readily identifiable vibrations $\nu(\text{P–Cl})$ can be used for the discrimination not only between 1,3,2-dioxaphospholanes and 1,3,2-dioxaphosphorinanes, but also between these cyclic and corresponding acyclic compounds.

The vibrations of the PCl_2 group (see Table 16) have marked spectral indications. Symmetrical stretching vibrations $\nu_s(\text{PCl}_2)$ of the molecules of alkyl phosphorodichloridites appear as very strong IR absorption bands and Raman lines in the region $\sim 490\text{--}510\text{ cm}^{-1}$. The less intense peaks in the region $\sim 440\text{--}480\text{ cm}^{-1}$ are associated with antisymmetric vibrations. Identification of these vibrations using the Raman spectra is facilitated by the fact that the lines corresponding to $\nu_s(\text{PCl}_2)$ are strongly polarised while those corresponding to $\nu_{as}(\text{PCl}_2)$ are depolarised or nearly depolarised. It should be noted that the appearance of additional intense peaks in these spectral regions, which are due to the deformation vibrations of non-branched alkoxy groups at the phosphorus atom (see Table 16) prevents easy interpretation.

The deformation vibration of the PCl_2 group is also characteristic of alkyl phosphorodichloridites. The corresponding line is observed in the region $\sim 190\text{--}220\text{ cm}^{-1}$ and can be identified with ease in the Raman spectra, since it is always strong and has a depolarisation ratio of about 0.6.

It should be noted that vibrational spectra of phosphorochloridites change as the state of aggregation of compounds under study changes or on dissolution, which is mainly due to intermolecular interactions. The frequencies of the vibrations involving the P–Cl bonds change to the greatest extent. All the above-mentioned characteristic spectral regions refer to the spectra of neat liquids at room temperature.

VI. Dialkylphosphoramidites

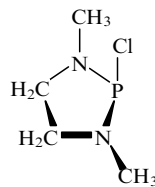
To date, a normal coordinate analysis has been performed only for four compounds containing $\text{Alk}_2\text{NP}^{\text{III}}$ groups. The simplest molecules, such as dimethylphosphoramidodifluoridite

(**40**)^{114–116} and dimethylphosphoramidodichloridite (**41**),¹¹⁷ adopt single conformations. The structure of molecule **40** was studied by X-ray analysis,¹¹⁸ gas-phase electron diffraction,¹¹⁹ and microwave spectroscopy.^{116,120} However, two structures of the (CH₃)₂NP fragment were proposed, a planar¹¹⁸ and a pyramidal one.¹¹⁹ Later, the results obtained in the former study¹¹⁹ were critically reviewed^{116,120} since structural parameters of the molecule **40** obtained in more recent studies appeared to be in agreement with the data of the X-ray study.¹¹⁸ The results of gas-phase electron diffraction investigations^{121–123} of molecules **41**, [(CH₃)₂N]₂PCl (**42**) and 2-chloro-1,3-dimethyl-1,3,2-diazaphospholane (**43**) also suggested that the dialkylamino group at the trivalent phosphorus atom has a nearly planar structure. It was found that this group in the molecule **40** is oriented parallel to the LEP of the phosphorus atom.^{116,118,120} Based on the results obtained in studies on the vibrational¹¹⁷ and NMR spectra,¹²⁴ a similar conformation was suggested for the molecule of compound **41**. At the same time, it was stated¹²¹ that the (CH₃)₂NP group is oriented perpendicular to the LEP of the phosphorus atom. Spectra of molecules **40**, **41** and fully deuterated derivative of compound **41** have been studied^{114,117} and a normal coordinate analysis was performed¹²⁵ for the conformations with eclipsed arrangement of the plane of the dimethylamino groups and the LEP of the phosphorus atom. It was also assumed that the molecules have no symmetry elements because of the non-symmetrical orientation of methyl groups.

The initial empirical interpretation of the spectra of dimethylphosphoramidodifluoridite **40** (see Ref. 117) was essentially different from that based on the results of normal coordinate analysis (see Ref. 125). In addition, the experimental vibrational spectra reported by Durig and Casper¹¹⁷ contained some 'extra' Raman lines and IR absorption bands as compared with the spectra reported earlier.¹¹⁴ Probably, they are due to impurities formed as a result of partial hydrolysis. Because of this, Table 18 lists the experimental results¹¹⁴ interpreted on the basis of normal coordinate analysis.¹²⁵ After publication of the study cited (Ref. 125), new spectra of dimethylphosphoramidodifluoridite **40** and its

D-isotopomers have been reported,¹¹⁶ which are somewhat different from those published previously.¹¹⁴

The molecules of tetramethylphosphorodiamidochloridite and 2-chloro-1,3-dimethyl-1,3,2-diazaphospholane adopt single conformations.^{126,127} The equilibrium conformation of the molecule **43** has a C_s symmetry (see Refs 123, 127).



The vibrational spectra of compound **42** (Table 19) have been interpreted¹²⁷ assuming that both dimethylamino groups in the molecule are arranged so that they are nearly eclipsed by the LEP of the phosphorus atom. The results of normal coordinate analysis for this conformer with C_s symmetry are in good agreement with experimental data.¹²⁷ At the same time, it should be noted that, according to the electron diffraction data,¹²² molecule **42** has a non-symmetrical conformation. The spectra of compound **43** listed in Table 20 are given in accordance with the known interpretation.¹²⁷

Analysis of the spectra of phosphoramides based on the results of normal coordinate analysis (see Table 18–20) made it possible to establish the nature of the bands characteristic of the (CH₃)₂NP group. It is known^{1–5} that the bands of medium or high intensity in the frequency range ~ 1260–1320 cm^{–1} are observed in the IR spectra of compounds with these groups. These bands are associated with the vibration in which a symmetric stretch of both N–C bonds [the ν_s(NC₂) vibration] is accompanied by contraction of the P–N bond [the ν(P–N) vibration]. The frequency of synchronous stretch of the three bonds lies in the range ~ 650–700 cm^{–1}. The corresponding IR absorption bands

Table 18. Interpretation of vibrational spectra of dimethylphosphoramidodifluoridite.

No.	Assignment	Raman (l)	IR (g)
13	$r(\text{CH}_3)$, $\nu(\text{PN})$, $\nu_s(\text{NC}_2)$, $\delta(\text{NC}_2)$	1306, m, p	1307, m
14	$\nu_{\text{as}}(\text{NC}_2)$, $r(\text{CH}_3)$		1195, m
15	$r(\text{CH}_3)$	1103, vw	
16	$r(\text{CH}_3)$	1071, w, dp?	1073, w
17	$r(\text{CH}_3)$, $\nu_{\text{as}}(\text{NC}_2)$		1002, sh ^a
18	$\nu_{\text{as}}(\text{PNC})$, $r(\text{CH}_3)$	989, m, dp?	989, s
19	$\nu_s(\text{PF}_2)$	792, m, p?	814, s
20	$\nu_{\text{as}}(\text{PF}_2)$	743, m, dp?	770, s
21	$\nu_s(\text{NC}_2)$, $\nu(\text{PN})$	705, vs, p	704, m
22	$\delta(\text{PF}_2)$, $r(\text{NC}_2)$	495, m	501, w, br
23	$\delta(\text{NC}_2)$, $\delta(\text{PF}_2)$	393, w	
24	$t(\text{PF}_2)$, φ ^{b,c}	393, w	
25	$r(\text{NC}_2)$, $\delta(\text{PF}_2)$	336, m	
26	$w(\text{PF}_2)$, $r(\text{NC}_2)$	239, w	
27	φ , ^b χ ^b	173, w	
28	χ , ^b φ ^{b,d}	97, vw	

^a From the spectrum of crystals.

^b The character φ denotes the out-of-plane deviation of the P–N bond with respect to the CNC plane and the character χ denotes torsional vibrations about the P–N bond.

^c A strong band at 343 cm^{–1} in the IR spectrum and a weak Raman line at 346 cm^{–1} in the spectra of low-temperature crystals were also associated with this vibration.¹¹⁶

^d Weak peaks at ~ 116 cm^{–1} in the IR spectra were also associated with this vibration.¹¹⁶

Table 19. Interpretation of vibrational spectra of tetramethylphosphoramidochloridite.

No.	Symmetry	Assignment	Raman (l)	IR (l) ^a
13	A'	$r(\text{CH}_3)$, $\nu(\text{PN}) - \nu_s(\text{NC}_2)$		1280, sh
41	A''	$r(\text{CH}_3)$, $\nu(\text{PN}) - \nu_s(\text{NC}_2)$	1275, 6, 0.3	1271, s
14	A'	$\nu_{\text{as}}(\text{NC}_2)$, $r(\text{CH}_3)$	1185, vw	1192, s
42	A''	$\nu_{\text{as}}(\text{NC}_2)$, $r(\text{CH}_3)$	1140, vw, 0.8	1140, w
43	A''	$r(\text{CH}_3)$	1090, vw	1095, w
15	A'	$r(\text{CH}_3)$		1082, vw
16	A'	$r(\text{CH}_3)$	1060, 6, 0.8	1061, m
44	A''	$r(\text{CH}_3)$		1029, vs
17	A'	$r(\text{CH}_3)$		1029, vw
45	A''	$r(\text{CH}_3)$		1029, vs
46	A''	$\nu_s(\text{NC}_2) - \nu(\text{PN})$, $r(\text{CH}_3)$	980, 9, 0.8	980, vs
18	A'	$\nu_s(\text{NC}_2) - \nu(\text{PN})$, $r(\text{CH}_3)$	960, 7, 0.8	960, vs
47	A''	$\nu_s(\text{NC}_2) + \nu(\text{PN})$	695, w, sh	698, s
19	A'	$\nu_s(\text{NC}_2) + \nu(\text{PN})$	670, 100, 0.12	671, m
20	A'	$\nu(\text{PCL})$, $r(\text{NC}_2)$	490, vw	488, m, br
21	A'	$\nu(\text{PCL})$, $\delta(\text{PN}_2)$	410, 9, 0.4	415, m, br
48	A''	$\delta(\text{PN}_2)$, $w(\text{NC}_2)$	410, 9, 0.4	
22	A'	$\nu(\text{PCL})$, $w(\text{NC}_2)$	385, 6, 0.4	
49	A''	$r(\text{NC}_2)$, $w(\text{NC}_2)$	385, 6, 0.4	
23	A'	$\nu(\text{PCL})$, $\delta(\text{NC}_2)$	335, 67, 0.25	
50	A''	$r(\text{NC}_2)$, $\delta(\text{NC}_2)$	335, 67, 0.25	
24	A'	$w(\text{NC}_2)$, $\chi(\text{N}-\text{CH}_3)$	292, 52, 0.3	
51	A''	$w(\text{NC}_2)$, $\chi(\text{N}-\text{CH}_3)$	292, 52, 0.3	
52	A''	$w(\text{NC}_2)$	125, 3.7, dp	

^a Spectral region below 400 cm^{–1} has not been recorded.

Table 20. Interpretation of vibrational spectra of 2-chloro-1,3-dimethyl-1,3,2-diazaphospholane.

No.	Symmetry	Assignment	Raman (l)	IR (l) ^a
10	A'	$\nu(\text{CH}_2)$, $\nu(\text{P}-\text{N})$	1250, 1.6, p	
11	A'	$\nu(\text{N}-\text{CH}_3)$, $\nu(\text{CH}_2)$	1238, 1.8, p	1235, s
36	A''	$\nu(\text{N}-\text{CH}_3)$, $\nu(\text{CH}_2)$		1217, s
37	A''	$\nu_{\text{as}}(\text{PNCH}_3)$, $\nu(\text{CH}_2)$	1205, 2.9, dp	1205, w, sh
12	A'	$\nu_{\text{as}}(\text{PNCH}_3)$, $\nu(\text{CH}_2)$	1180, 3.3, p	1180, vw
13	A'	$\nu(\text{N}-\text{CH}_2)$, $\nu(\text{CH}_3)$, $\nu(\text{CH}_2)$		1148, s
38	A''	$\nu(\text{N}-\text{CH}_2)$, $\nu(\text{CH}_3)$, $\nu(\text{CH}_2)$	1125, 1.6, 0.7	
39	A''	$\nu(\text{CH}_3)$	1085, 0.8, 0.8	
14	A'	$\nu(\text{CH}_3)$		1055, w
15	A'	$\nu(\text{CH}_3)$, $\nu(\text{C}-\text{C})$	1030, 9.5, 0.4	1030, s
40	A''	$\nu(\text{CH}_2)$	1012, sh, dp	1010, m
41	A''	$\nu(\text{N}-\text{CH}_2)$	948, 2, 0.7	946, s
16	A'	$\nu(\text{N}-\text{CH}_2)$, $\nu(\text{C}-\text{C})$	855, 1.4, 0.8	855, br, sh
17	A'	$\nu(\text{CH}_2)$	830, 0.3	
18	A'	ν pulse	710, 100, 0.08	706, m
42	A''	$\nu(\text{P}-\text{N})$	692, sh	692, m
43	A''	ring δ	597, 10.5, 0.86	595, w
19	A'	$\nu(\text{P}-\text{Cl})$, $\nu(\text{P}-\text{Cl})$	490, 18.4, 0.34	490, m
20	A'	$\nu(\text{P}-\text{Cl})$	392, 12.6, 0.3	
44	A''	$\nu(\text{N}-\text{CH}_3)$	355, 11, 0.83	
45	A''	$\gamma(\text{N}-\text{CH}_3)$, ring χ	310, sh	
21	A'	ring δ	300, 29.5, p	
22	A'	$\nu(\text{N}-\text{CH}_3)$	268, 27.9, 0.25	
46	A''	$\chi(\text{N}-\text{CH}_3)$	245, br, sh	
25	A'	$\gamma(\text{N}-\text{CH}_3)$	112, 30, 0.6	

^a Spectral region below 400 cm^{-1} has not been recorded.

are, as a rule, rather weak, while the Raman lines are intense and strongly polarised.

The vibration $\nu_{\text{as}}(\text{NC}_2)$ with predominant contributions of the antiphase stretch and tension of the N—C bonds interacts with the stretching vibration $\nu(\text{P}-\text{N})$. One of the two resultant vibration appears as a band of strong or medium intensity in the IR spectrum in the region 1140–1210 cm^{-1} . For the trivalent phosphorus compounds, this band is shifted towards high frequencies in this spectral region. The other resultant vibration gives rise to a strong IR absorption band¹ in the region ~ 935–1008 cm^{-1} (a narrower spectral region ~ 940–980 cm^{-1} has also been reported^{4,5}). The corresponding Raman lines are usually weak, as are the lines corresponding to the $\nu(\text{CH}_3)$ rocking vibrations, which appear in the IR spectra of molecules containing the $(\text{CH}_3)_2\text{NP}$ groups as bands of medium intensity in the frequency range ~ 1050–1080 cm^{-1} .

Two or even three peaks can be observed in these spectral regions for diamides and triamides (see Tables 19, 20). The bands due to the vibrations with the contributions of the vibrations $\nu(\text{P}-\text{N})$ and $\nu_{\text{as}}(\text{NC}_2)$ in the frequency range 1140–1210 cm^{-1} or the vibration $\nu_{\text{as}}(\text{NC}_2)$ in the frequency ranges 935–1008 and 650–700 cm^{-1} are mainly split. The splitting is to a great extent caused by the kinematic interaction between the dimethylamino groups through the shared phosphorus atom.¹²⁷

It is of interest to compare the spectra of acyclic compound **42** (see Table 19) and its cyclic analogue **43** (see Table 20). A distinctive feature of the vibrational spectra of 2-chloro-1,3-dimethyl-1,3,2-diazaphospholane **43** is that they contain the lines at 1370, 1342 and 830 cm^{-1} corresponding to the methylene groups, as well as the lines at 855 and 597 cm^{-1} caused by the ring vibrations. As in the case of acyclic compound **42**, the strongest line in the Raman spectrum of the phospholane **43** is associated with the totally symmetrical vibration with the contribution of the P—N bonds. However, for compound **43** the frequency of this line (710 cm^{-1}) is shifted as compared with that of tetramethylphosphoramidochloridite **42** (670 cm^{-1}), whereas

the frequencies of the corresponding antisymmetrical vibrations (692 cm^{-1}) remain virtually unchanged.

VII. Phosphorothioites

A rather large number of studies dedicated to the interpretation of the spectra of phosphorothioites has been reported. Normal coordinate analyses were performed for cyclic and acyclic molecules with one, two and three RSP groups, where R are various alkyl, dithiocarbamoyl and dithiophosphoryl radicals. The simplest representative of phosphorothioites, methyl phosphorodichloridithioite (**44**), exists in the liquid and gas phases as a mixture of the *T* and *G* conformers (see Fig. 1; X = Cl, Y = S, Z = CH₃).^{103, 128} Vibrational spectra of compound **44** have been interpreted¹²⁹ assuming that the molecule adopts a single conformation. Then, it was established¹⁰³ that the molecule adopts several conformations, the previous assignments¹²⁹ were refined and a normal coordinate analysis was performed for the spectrum of compound **44**. These results are listed in Table 21.

Table 21. Interpretation of vibrational spectra of methyl phosphorodichloridithioite.^a

No.	Symmetry	Assignment	Raman (l)	IR (l) ^b
7	A'	$\nu_s[\text{PCl}_2(\text{G})]$	516, m	520, sh
		$\nu_s(\text{PCl}_2)$	496, m	496, s, br
		$\nu_{\text{as}}[\text{PCl}_2(\text{G})]$	481, sh	
15	A''	$\nu_{\text{as}}(\text{PCl}_2)$	474, s	472, s
8	A'	$\nu(\text{P}-\text{S})$	461, m	466, s, br
9	A'	$\delta(\text{PSC})$	318, s	
		$\delta[\text{PSC}(\text{G})]$	262, s	
16	A''	$\nu(\text{PCl}_2)$	202, vs	
10	A'	$\delta(\text{PCl}_2)$	185, m	
		$\nu[\text{PCl}_2(\text{G})]$	168, w	
11	A'	$\nu(\text{PCl}_2)$	150, sh	

^a See note to Table 2. ^b Spectral region below 400 cm^{-1} has not been recorded.

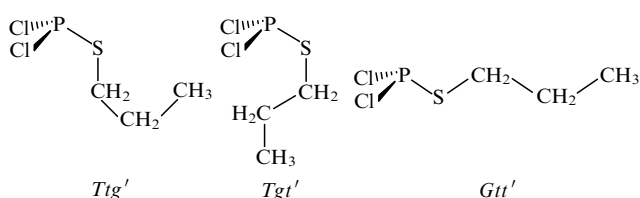
The molecule of ethyl phosphorodichloridithioite (**45**) can adopt five stable conformations¹³⁰ (see Fig. 2; X = Cl, Y = S). Vibrational spectra of compound **45** have been interpreted using the results of normal coordinate analysis.¹³⁰ It has been shown that internal rotation about both the P—S and S—C bonds occurs in the neat liquid and in solutions. However, it was not established whether the *Gg* and *Gg'* conformations or at least one of them do exist (we only can say that the existence of these conformers does not contradict experimental data). Keeping this in mind, the spectra of ethyl phosphorodichloridithioite **45** can be interpreted in different ways, since some of the frequencies can be attributed to either the *Tg* conformers or the *Tg*, *Gg* and *Gg'* conformers simultaneously. These frequencies are denoted by a character 'g'. The bands, which can be attributed to the *Gt*, *Gg* and *Gg'* conformers are denoted by a character 'G'. A version^{130, 131} of the interpretation of the spectra of compound **45** is listed in Table 22.

The molecule of propyl phosphorodichloridithioite (**46**) can adopt 14 spectroscopically discernible conformations, of which three are shown in Fig. 4. It was established that the *T*, *G*, *gt'*, *tt'*, *gg'* and *tg'* conformers of the molecule **46** (for the meaning of notations, see Fig. 4) exist in the liquid and in solutions and a normal coordinate analysis was performed for all possible conformers.¹³² Attempts to establish exact composition of such a complex mixture of conformers have failed.

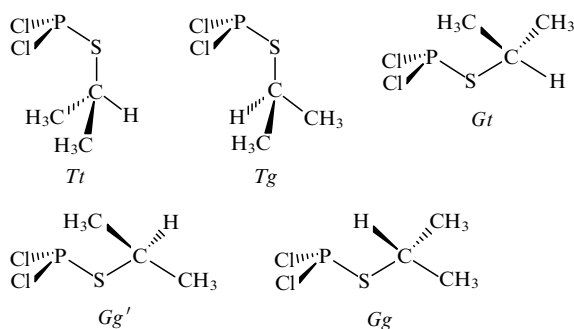
The molecule of isopropyl phosphorodichloridithioite (**47**) can adopt five spectroscopically discernible conformations (Fig. 5). The bands associated with internal rotation about the P—S and S—C bonds of the molecule are observed in the vibra-

Table 22. Interpretation of vibrational spectra of ethyl phosphorodichloridothioite.^a

No.	Symmetry	Assignment	Raman (l)	IR (l) ^b
22	A''	$r[\text{CH}_2(g)]$		780, vw
10	A'	$r(\text{CH}_2)$	765, l	765, w
		$\nu(\text{SC}), \delta(\text{SCC}), \delta(\text{PSC})$	655, 18, p	655, w
		$\delta(\text{SC}), \delta(\text{SCC}), \delta[\text{PSC}(g)]$	645, 21, p	645, w
		$\nu_s[\text{Cl}_2\text{PS}(G)]$	510, 36, p	514, vs
11	A'	$\nu_s(\text{Cl}_2\text{PS})$	500, sh, p	500, vs
12	A'	$\nu_s(\text{PCl}_2), \nu(\text{P}-\text{S})$	474, 100, p	476, vs
		$\nu_{as}[\text{PCl}_2(Tg, Gt, Gg, Gg)]$	493, sh, dp	
23	A''	$\nu_{as}(\text{PCl}_2)$	460, sh, dp	
		$\delta(\text{SCC}), \delta[\text{PSC}(g)]$	340, 11, p	
13	A'	$\delta(\text{SCC}), \delta(\text{PSC})$	320, 4, p	
14	A'	$\delta(\text{PSC}), \delta(\text{SCC})$	260, 27, p	
		$\delta(\text{PSC}), \delta[\text{SCC}(G)]$	248, 32, p	
24	A''	$r(\text{PCl}_2)$	190, 44, dp	
15	A'	$\delta(\text{PCl}_2)$		
16	A'	$w(\text{PCl}_2), \delta(\text{SCC})$	135, 10, p	

^a See note to Table 3.^b Spectral region below 400 cm⁻¹ has not been recorded.**Figure 4.** Conformers of the molecule of propyl phosphorodichloridothioite:

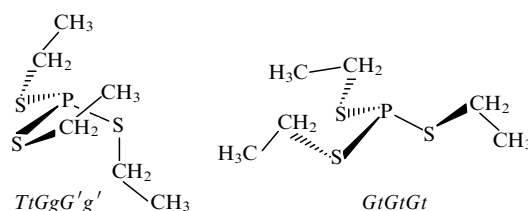
Ttg' stands for *trans,trans,gauche*, *Tgt'* for *trans,gauche,trans* and *Gtt'* for *gauche,trans,trans*; *T* and *G* denote the *trans* and *gauche* conformers formed owing to rotation about the P-S bond; *t* and *g* denote the *trans* and *gauche* conformers formed owing to rotation about the S-C bond and *t'* and *g'* denote the *trans* and *gauche* conformers formed owing to rotation about the C-C bond.

**Figure 5.** Conformers of the molecule of isopropyl phosphorodichloridothioite:

Tt stands for *trans,trans*, *Tg* for *trans,gauche*, *Gt* for *gauche,trans*, *Gg* for *gauche,gauche* and *Gg'* for *gauche,gauche'*.

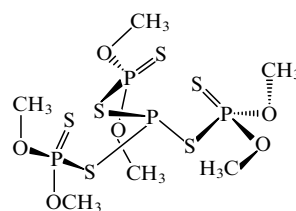
tional spectra of liquid **47**.¹³² Only the *Tg* conformer is retained upon crystallisation.

The number of possible conformers of the molecule of triethyl phosphorothioite (**48**) is as large as 36. Nevertheless, experimental spectra of neat (liquid) compound **48** and its solutions can be interpreted¹³⁰ assuming that its molecule has only two conformers.

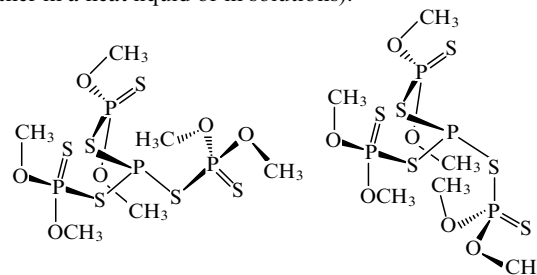


Here, the first two characters denote the conformation of one C₂H₅SP group of the molecule **48**, while the next two pairs of characters denote the conformations of the other two identical groups. It has been reported that only the *TtGgG'g'* conformer is retained upon crystallisation.¹³⁰

In the crystalline phase, the equilibrium conformation of the molecule of *S,S',S''*-tris(dimethoxythiophosphoryl) phosphorotrithioite (**49**) has a C₃ symmetry (see Ref. 133)

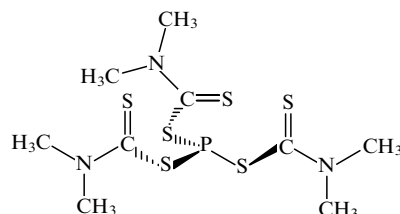


Other, non-symmetrical conformers appear in the liquid phase (either in a neat liquid or in solutions).¹³⁴



This gives rise to additional peaks in the spectra. Normal coordinate analysis for all possible conformers of the molecule **49** shows¹³⁴ that additional bands can be attributed to the non-symmetrical conformers. Some bands were assigned to those conformers which can be formed from all the three conformers shown above by changing the arrangement of the methoxy groups of the (CH₃O)₂P(=S) fragment from *gauche'*, *gauche* with respect to the P= S bond to the *gauche,gauche* or *gauche,trans* with respect to the same bond. The presence of other conformers also does not contradict the results of spectral experiments.¹³⁴

The equilibrium conformation of the molecule of *S,S',S''*-tris(*N,N'*-dimethylthiocarbamoyl) phosphorotrithioite (**50**) in the crystalline phase has a C₃ symmetry group (see Ref. 135).



According to the vibrational spectroscopy data,¹³⁶ the molecule of compound **50** in solutions retains a single conformation.

According to the results of the gas-phase electron diffraction study,¹³⁷ the molecule of 2-chloro-1,3,2-dithiaphospholane (**51**) adopts a symmetrical 'envelope' conformation with an apical phosphorus atom and an axial P-Cl bond. On the other hand, data obtained in the NMR¹³⁸ and vibrational spectroscopic¹⁰⁸ studies indicate that the molecule of compound **51** adopts a non-symmetrical conformation. Calculations by the molecular mechanics method predict the *a-E_C* conformation of molecule **51**

Table 23. Interpretation of vibrational spectra of 2-chloro-1,3,2-dithiophospholane.

No.	Assignment	Raman (I)	IR (I) ^a
11	$\nu(\text{C}-\text{C})$	987, 0, 0.73	990, w
12	$r(\text{CH}_2)$	938, 0, 0.45	942, m
13	$r(\text{CH}_2)$, $\delta(\text{CCS})$	825, 0, 0.78	830, w
14	$\nu(\text{C}-\text{S})$, $\delta(\text{CCS})$, $r(\text{CH}_2)$	664, 10, 0.43	665, w
15	$\nu(\text{C}-\text{S})$, $\delta(\text{CCS})$	646, 50, 0.13	647, m, s
16	$\nu(\text{P}-\text{Cl})$, $\nu_s(\text{PS}_2)$	480, 100, 0.1	482, w, br
17	$\delta(\text{PSC})$, $\delta(\text{CCS})$	440, 40, 0.76	442, w
18	$\nu(\text{P}-\text{S})$, $\delta(\text{CCS})$	415, 40, 0.30	420, w, br
19	$\nu(\text{PS}_2)$	362, 50, 0.27	352, ms
20	$\delta(\text{PSC})$, $\delta(\text{SPS})$, $\delta(\text{SPCl})$	255, 10, 0.67	256, w
21	$\delta(\text{SPS})$, $\delta(\text{CCS})$	196, 30, 0.63	
22	$\delta(\text{SPCl})$	175, 40, 0.85	
23	ring puckering ^b	102, 20, 0.78	
24	ring puckering ^b	102, 20, 0.78	

^a Spectral region below 400 cm^{-1} has not been recorded.^b Nonplanar vibration.

(see Fig. 3; $\text{X} = \text{Y} = \text{S}$). Table 23 lists the interpretation of the vibrational spectra of 2-chloro-1,3,2-dithiaphospholane **51** for this conformation.¹⁰⁸ Experimental spectral parameters¹⁰⁸ of liquid compound **51** coincide with previously reported data,¹³⁹ except for the degrees of depolarisation of the Raman lines.

Stretching vibrations of the $\text{P}-\text{S}$ and $\text{S}-\text{C}$ bonds are most pronounced in the spectra of all the above-mentioned alkyl phosphorothioites. The vibrations $\nu(\text{S}-\text{C})$ can mix with the deformations of the alkylthio group and PSC fragment (Table 24), which is responsible for the variations in the intensities of the corresponding IR absorption bands (from weak to medium) and Raman lines (from medium to strong). The phosphorus-containing fragment of the molecule contributes negligibly to the potential energy of this vibration, therefore its frequency depends on the structure of the alkylthio group. Because of this, the $\nu(\text{S}-\text{C})$ 'fingerprint' spectral regions⁸⁷ of phosphorothioites nearly coincide with those of different organosulfur compounds. It is more convenient to identify stretching vibrations of the $\text{S}-\text{C}$ bond using the Raman spectra, since the corresponding lines are rather strong and polarised. If internal rotation of the alkylthio groups about the $\text{S}-\text{C}$ bond can lead to inequivalent orientations of these groups with respect to the $\text{P}-\text{S}$ bond, the Raman lines become multiplets.

It is also desirable to identify the $\text{P}-\text{S}$ bonds using the Raman spectroscopy. The stretching vibrations $\nu(\text{P}-\text{S})$ in the molecules of alkyl phosphorodichloridothioites are strongly coupled with symmetrical stretching vibrations of the PCl_2 group. One of the two resultant vibrations appears as strong bands in the IR spectrum and polarised Raman lines of medium or strong intensity in the region $\sim 490-530 \text{ cm}^{-1}$. The second vibration is associated with very strong polarised Raman lines and strong IR absorption bands in the region $\sim 460-480 \text{ cm}^{-1}$. If the molecules of compounds under study can adopt several conformations, all these bands are, as a rule, multiplets; it is noteworthy that polarised Raman lines can have depolarised 'shoulders'.

The vibrations $\nu(\text{P}-\text{S})$ can also interact with vibrations of other groups at the phosphorus atom (see Table 24). Nevertheless, the presence of both a strong polarised Raman line and an IR absorption band of medium or strong intensity in the region $\sim 470-540 \text{ cm}^{-1}$ can be considered to be a reliable spectral indicator of the single $\text{P}-\text{S}$ bond, while multiplet IR and Raman spectra in this spectral region can be regarded as an indicator of the existence of different conformers due to the internal rotation about this bond. This spectral region is characteristic of acyclic molecules. For cyclic phosphorothioites, the frequencies of the stretching vibrations $\text{P}-\text{S}$ can be substantially lower.

Table 24. Vibrations of fragments of the molecules with contributions of the $\text{P}-\text{S}$, $\text{P}-\text{Cl}$ and $\text{S}-\text{C}$ bonds in the spectra of organophosphorus compounds.

Molecule	Assignment	Raman (I)	IR (I)
CH_3SPCl_2	$\nu_s[\text{PCl}_2(G)]$	516, m	520, sh
	$\nu_s[\text{PCl}_2(T)]$	496, m	496, s, br
	$\nu_{as}[\text{PCl}_2(G)]$	481, sh	472
	$\nu_{as}[\text{PCl}_2(T)]$	474, s	
	$\nu(\text{P}-\text{S})$	461, m	466, s, br
$\text{C}_2\text{H}_5\text{SPCl}_2$	$\nu(\text{S}-\text{C})$, $\delta(\text{SCC})$, $\delta[\text{PSC}(t)]$	655, m, p	655, w
	$\nu(\text{S}-\text{C})$, $\delta(\text{SCC})$, $\delta[\text{PSC}(g)]$	645, m, p	645, w
	$\nu_s[\text{Cl}_2\text{PS}(G)]$	510, s, p	514, vs
	$\nu_s[\text{Cl}_2\text{PS}(T)]$	500, sh, p	500, vs
	$\nu_s(\text{PCl}_2)$, $\nu(\text{P}-\text{S})$	474, vs, p	476, vs
	$\nu_{as}[\text{PCl}_2(Tg, Gt, Gg)]$	493, sh, dp	
	$\nu_{as}[\text{PCl}_2(Tt)]$	460, sh, dp	
$n\text{-C}_3\text{H}_7\text{SPCl}_2$	$\nu(\text{S}-\text{C})$, $\delta[\text{SCC}(tt')]$	720, sh	
	$\nu(\text{S}-\text{C})$, $\delta[\text{SCC}(tg')]$	645, w, p	
	$\nu(\text{S}-\text{C})$, $\delta[\text{SCC}(gg')]$	635, w, p	
	$\nu_s[\text{Cl}_2\text{PS}(G)]$	510, s, p	
	$\nu_s[\text{Cl}_2\text{PS}(T)]$	500, sh	
	$\nu_s(\text{PCl}_2)$, $\nu(\text{P}-\text{S})$	475, vs, p	
	$\nu_{as}[\text{PCl}_2(Tg, Gt, Gg)]$	492, sh, dp	
	$\nu_{as}[\text{PCl}_2(Tt)]$	455, s, dp	
$\text{iso-C}_3\text{H}_7\text{SPCl}_2$	$\nu[\text{S}-\text{C}(g)]$	615, w, p	
	$\nu[\text{S}-\text{C}(t)]$	610, sh	
	$\nu_s[\text{Cl}_2\text{PS}(G)]$	527, s, p	
	$\nu_s[\text{Cl}_2\text{PS}(T)]$	505, sh, p	
	$\nu_s(\text{PCl}_2)$, $\nu(\text{P}-\text{S})$	475, vs, p	
	$\nu_{as}[\text{PCl}_2(G)]$	490, sh, dp	
	$\nu_{as}[\text{PCl}_2(T)]$	450, sh, dp	
	$\nu(\text{S}-\text{C})$, $\delta(\text{SCC})$, $\delta[\text{PSC}(t)]$	665, sh, 0.5	
	$\nu(\text{S}-\text{C})$, $\delta(\text{SCC})$, $\delta[\text{PSC}(g)]$	650, s, 0.3	650, w
	$\nu(\text{P}-\text{S})$, $r[\text{PCCl}(G)]$	498, vs, 0.1	503, m
	$\nu(\text{P}-\text{S})$, $r[\text{PCCl}(T)]$	482, sh, 0.3	486, m
	$\nu(\text{C}-\text{S})$, $\delta(\text{CCS})$, $\delta(\text{CCO})$	679, s, 0.35	680, w
	$\nu(\text{P}-\text{Cl})$	469, vs, br, 0.3	470, vs
	$\nu(\text{P}-\text{S})$	414, vs, br, 0.3	415, vs
	$\nu(\text{C}-\text{S})$, $\delta(\text{CCS})$, $r(\text{CH}_2)$	664, w, 0.4	665, w
	$\nu(\text{C}-\text{S})$, $\delta(\text{CCS})$	646, w, 0.1	647, ms
	$\nu(\text{P}-\text{Cl})$, $\nu_s(\text{PS}_2)$	480, vs, br, 0.1	482, w, br
	$\nu(\text{P}-\text{S})$, $\delta(\text{CCS})$	415, s, br, 0.3	420, w, br
	$\nu(\text{PS}_2)$	362, s, 0.3	352, ms
$(\text{C}_2\text{H}_5\text{S})_3\text{P}$	$\nu_{as}(\text{PS}_3)$	515, sh, p?	513, s
	$\nu_{as}(\text{PS}_3)$	485, s, dp?	485, vs
	$\nu_s(\text{PS}_3)$	485, vs, p	455, s
$[(\text{CH}_3\text{O})_2\text{P}(\text{S})\text{S}]_3\text{P}$	$\nu_s[\text{PS}_3(gg)]$, $\nu_s(\text{PS}_3)$	523, s ^a	523, m ^a
	$\nu_s(\text{PSP})$	498, vs, p ^a	498, sh ^a
	$\nu(\text{PVS})$	485, sh, dp ^a	485, w ^a
	$\nu_{as}(\text{PSP})$		
$[(\text{CH}_3)_2\text{NC}(\text{S})\text{S}]_3\text{P}$	$\nu_s(\text{PS}_3)$	483, s ^b	485, vw ^b
	$\nu_{as}(\text{PS}_3)$	464, s ^b	465, m ^b

^a Melt. ^b Crystals.

Effective coupling of the stretching vibrations of three $\text{P}-\text{S}$ bonds in the molecules of trialkyl phosphorotrithioites gives rise to three new resultant motions (see Table 24). Symmetrical

stretching vibrations of all the three P–S bonds of the PS₃ group appear in the spectral region $\sim 430\text{--}470\text{ cm}^{-1}$. The corresponding Raman lines are very intense and strongly polarised and the IR absorption bands are of medium or strong intensity. Two antisymmetric vibrations $\nu_{\text{as}}(\text{PS}_3)$ appear as very strong bands in the IR spectrum and strong Raman lines in the region $\sim 460\text{--}500\text{ cm}^{-1}$ and as peaks of medium intensity in the region $\sim 500\text{--}570\text{ cm}^{-1}$. All the above-mentioned vibrations can be ‘conformationally sensitive’, therefore some ‘extra’ peaks can be observed in these regions of the spectra of those trialkyl phosphorotrithioites which can exist as a mixture of conformers.

If the molecules of trialkyl phosphorotrithioites have a C_3 symmetry, both antisymmetric vibrations $\nu_{\text{as}}(\text{PS}_3)$ become degenerate, *i.e.*, have equal frequencies. This is the case for *S,S',S''*-tris-(*N,N*-dimethylthiocarbamoyl) phosphorotrithioite **50** (see Table 24), for which a singlet IR absorption band and a singlet Raman line corresponding to the vibration $\nu_{\text{as}}(\text{PS}_3)$ are observed. Unlike the spectra of trialkyl phosphorotrithioites, the frequency of symmetric vibration $\nu_s(\text{PS}_3)$ in these spectra is higher than that of antisymmetric vibration $\nu_{\text{as}}(\text{PS}_3)$ (~ 485 vs. $\sim 465\text{ cm}^{-1}$, respectively).

This also holds for compound **49** (see Table 24) that is, the $\nu_s(\text{PS}_3)$ frequency is as high as nearly 500 cm^{-1} , while the $\nu_{\text{as}}(\text{PS}_3)$ frequency is 485 cm^{-1} . According to Thomas,¹ the IR absorption bands and Raman lines characteristic of compounds with the P^{III}SP group are usually observed in nearly the same spectral region ($\sim 480\text{--}510\text{ cm}^{-1}$). As can be seen from the data listed in Table 24, they should be attributed to the stretching vibrations of this group.

VIII. Compounds with Si–P, Ge–P and P–P bonds

Silylphosphine (**52**), (trifluorosilyl)phosphine (**53**) and germlylphosphine (**54**) are rare examples of the trivalent phosphorus compounds with Group IV elements for which normal coordinate analysis has been performed. The spectra of compound **52** and its fully deuterated analogue have been interpreted.^{140, 141} Analysis of the spectra of both these molecules¹⁴¹ has led to some changes in the vibrational assignments suggested earlier.¹⁴⁰ Vibrational spectra of compound **53** and its fully deuterated analogue were interpreted using the results of normal coordinate analysis¹⁴² and the spectra of phosphine **54** and its three D-isotopomers were studied.¹⁴³

A salient feature of the vibrational spectra of silyl- and germlylphosphines is that they contain the peaks which correspond to the stretching vibrations $\nu(\text{Si–P})$ and $\nu(\text{Ge–P})$. The vibration $\nu(\text{Si–P})$ appears in the region $\sim 300\text{--}530\text{ cm}^{-1}$, while the vibration $\nu(\text{Ge–P})$ appears in the region $\sim 290\text{--}410\text{ cm}^{-1}$. Both stretching vibrations can mix with skeletal deformations of the molecules (Table 25). This probably results in substantial variations of the intensities of the corresponding peaks. The vibrations $\nu(\text{Si–P})$ in the molecules of acyclic organophosphorus compounds appear in a somewhat narrower spectral region $\sim 380\text{--}530\text{ cm}^{-1}$. The vibrations $\nu_{\text{as}}(\text{PH}_2)$, $\nu_s(\text{PH}_2)$, $\delta(\text{PH}_2)$, characteristic of all primary phosphines, appear in the spectra of compounds under consideration in nearly the same way as in the spectra of alkylphosphines. For primary phosphines, the $\nu(\text{PH}_2)$ frequencies are somewhat higher while the $\delta(\text{PH}_2)$ frequencies are somewhat lower than those indicated in Section II.

In Table 25, the frequencies of these characteristic vibrations of the phosphino group are also given for the molecule of diphosphane (**55**). As can be seen, the frequencies of stretching and deformation vibrations of the PH₂ groups of the molecule **55** lie far beyond the limits of the spectral regions characteristic of alkyl-, silyl- and germlylphosphines and their halogen-substituted derivatives.

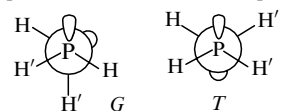
Only the *G* conformers have been detected in diphosphane **55** (see Refs 144–146). Vibrational spectra of diphosphane have been studied.^{144, 147–149} Table 25 lists the interpretation¹⁴⁴ of the

Table 25. Spectral indications of characteristic vibrations of molecules X_nAPY_m (A = Si, Ge, P).

Molecule	Assignment	Raman	IR
H ₃ SiPH ₂	$\nu_{\text{as}}(\text{PH}_2)$		2312 (g)
	$\nu_s(\text{PH}_2)$		2312 (g)
	$\delta(\text{PH}_2)$		1072 (g)
	$\nu(\text{Si–P})$		454 (g)
F ₃ SiPH ₂	$\nu_{\text{as}}(\text{PH}_2)$		2318, s (g)
	$\nu_s(\text{PH}_2)$	2310, s (l)	2312, s (g)
	$\delta(\text{PH}_2)$	1062, vw (l)	1069, s (g)
	$\nu(\text{Si–P}), \delta_s(\text{SiF}_3)$	507, vs (l)	512, vs (g)
H ₃ GePH ₂	$\nu_{\text{as}}(\text{PH}_2)$	2304, dp (l)	2320, s (g)
	$\nu_s(\text{PH}_2)$	2293, p (l)	2310, s (g)
	$\delta(\text{PH}_2)$		$\begin{cases} 1080, \text{R mw (g)}^a \\ 1065, \text{P vw (g)}^a \end{cases}$
	$\nu(\text{Ge–P}), w(\text{PH}_2)$	363, p	$\begin{cases} 371, \text{R?} \\ 352, \text{P?} \end{cases}$
H ₂ PPH ₂	$\nu_{\text{as}}(\text{P–H})$		2299, vs (cr)
	$\nu_s(\text{P–H})$	2295, vs (cr)	2312, vs (g)
	$\nu_{\text{as}}(\text{P–H}')^b$	2320, vs (g)	2281, vs (cr)
	$\nu_s(\text{P–H}')^b$	2268, vs (cr)	
	$\delta(\text{PH}_2), \delta(\text{PPH}) (\text{B})^c$	1054, s (cr)	1081 (g)
	$\delta(\text{PH}_2), \delta(\text{PPH}) (\text{A})^c$	1037, s (cr)	
	$\nu(\text{P–P})$	438, s (g)	
I ₂ PPI ₂	$\nu(\text{P–P}), \nu(\text{P–I})$	319, vw (cr)	
	$\nu(\text{P–I}), \nu(\text{P–P})$	307, vs (cr)	
(CF ₃) ₂ PP(CF ₃) ₂	$\nu(\text{P–P}), \nu_s(\text{PC}_2)$	486, m, p (l)	~ 497 , vw (g)

^a Characters R and P denote the branches of the contours of the IR absorption bands.

^b The meaning of notation H' is clearly seen from the Newman projections of possible conformations of diphosphane and its derivatives:



^c Symmetry species of vibrations.

spectra, which is based on the results of normal coordinate analysis for molecules **55** and P₂H₂D₂. Vibrational assignments made in the framework of *ab initio* calculations¹⁴⁶ of the force field of the molecule **55** differ only slightly from those listed above.

Initially, the spectra of solutions of tetraiododiphosphane (**56**) were interpreted assuming the *gauche* conformation of the molecule.¹⁵⁰ However, it was shown later¹⁵¹ that the *trans* conformation exists in fact both in the crystal and in solutions. Taking into account the results of normal coordinate analysis of the molecule **56** (see Ref. 152), some vibrational assignments in the low-frequency region were changed compared to those reported earlier.¹⁵⁰

Vibrational spectra of tetrakis(trifluoromethyl)diphosphane (**57**) have been interpreted¹⁵³ assuming that the molecule **57** has only the *trans*-conformation with a C_{2h} symmetry. Under this symmetry group, the vibrations of the A_g and B_g types should be Raman active while the vibrations of the A_u and B_u types should be IR active (the so-called principle of alternative exclusion). However, the results of spectroscopic studies¹⁵³ indicate that this principle is not obeyed. The fact that the IR absorption band corresponding to the vibration $\nu(\text{P–P})$ (see Table 25) is weak is not always a consequence of alternative exclusion. It is known that these bands can also be of weak intensity if the molecules with the P–P bond adopt non-symmetrical conformations. Therefore, the conclusion¹⁵³ that the molecule **57** has a C_{2h} symmetry, which is based on the weak intensity of the $\nu(\text{P–P})$ band, casts some doubts. Correspondingly, the results of theoretical interpretation of the spectra¹⁵³ can appear to be not sufficiently rigorous.

It is convenient to identify the P–P bond in diphosphanes using Raman spectra where the line corresponding to the vibration $\nu(\text{P}–\text{P})$ is observed in the region $\sim 300–530\text{ cm}^{-1}$, has a medium or strong intensity and is polarised (for gases, liquids or solutions).

IX. Rotational isomerism of trivalent phosphorus compounds and its manifestation in vibrational spectra

1. General

If interconversions between stable conformations of a molecule can occur owing to hindered internal rotation and if the conformers are not mirror images, their vibrational frequencies can differ from one another. Because of this, the number of bands and lines in the vibrational spectra of organophosphorus compounds, whose molecules can adopt several conformations, is larger than it should be expected for a single molecular conformation. As a rule, the ‘sensitivity’ to rotations of a particular molecular fragment about an X–Y bond with respect to another molecular fragment is characteristic of those vibrations to which the bond in question contributes. Usually, the frequencies of other vibrations depend only slightly on the molecular conformation, so that the corresponding IR absorption bands or Raman lines in the spectra of different conformers coincide. Therefore, an equilibrium between N conformers rarely, if ever, leads to the N -fold increase in the number of spectral peaks; rather, it causes multiplet splittings of particular peaks, e.g., the $\nu(\text{X}–\text{Y})$ or $\delta(\text{XYZ})$ peaks. However, the frequencies of vibrations with predominant contribution by a particular molecular fragment can also be dependent on the conformation of another molecular fragment. This dependence is due to changes in either or both the spatial mass distribution and the force constants of the molecule on interconversions between different conformations. Sometimes, the effect of conformations on the vibrational frequencies is so weak that it can be detected only in the low-temperature experiments. In this case, the spectral contours become much narrower and the peaks of different conformers which have been unresolved at room temperature, can be observed as multiplets or as separated bands. In other cases, shifts in the vibrational frequencies due to conformational effects are as large as tens of cm^{-1} . Usually, crystallisation leads to simplification of the conformational composition of most compounds and disappearance of particular spectral bands. The conformational composition depends also on the temperature and polarity of the medium. Therefore, the conditions of spectroscopic experiments can strongly affect the spectra of organophosphorus compounds, whose molecules can adopt several conformations. This should be taken into account when interpreting the spectra.

For instance, the intensities of the bands of conformers of greater polarity usually increase in polar media and decrease on going to non-polar solutions. This correlation can be used for the assignment of spectral peaks to the conformers of different polarities. However, the assignments based on both the experimental results and the results of normal coordinate analysis for possible conformers are the most reliable. It is these vibrational assignments that are generalised in this review and serve as the basis for simple empirical rules which facilitate the interpretation of the spectra of organophosphorus compounds, whose molecules can adopt several conformations.

2. Internal rotation of Alk–P fragments

Alkylphosphines and their derivatives with the general formula AlkPX_2 (Alk = C_2H_5 , $n\text{-C}_3\text{H}_7$, $\text{iso-C}_3\text{H}_7$; X = H, F, Cl, CH_3), which are liquids or gases at room temperature, are characterised by the existence of an equilibrium between the G and T conformers formed owing to internal rotation about the P–C bond (see Figs 1, 2). The T conformers are more energetically favourable than the G conformers,^{15–21, 23, 56–61} except for the molecule of ethyl(dimethyl)phosphine;^{46, 154, 155} the energy ‘gain’ is nearly

1.6 kJ mol^{-1} in the liquid phase and 0.8 kJ mol^{-1} in the gas phase. It should be noted that the enthalpy differences (ΔH) between the T and G conformers are small: they vary from ~ 0.4 to $\sim 4.2\text{ kJ mol}^{-1}$ and decrease on going from the liquid to the gas phase. Therefore, liquid or gaseous alkylphosphines exist at room temperature as mixtures of the G and T conformers in comparable proportions.

Many of the vibrations of the T and G conformers have different frequencies (see Tables 2–4). The simplest rule is valid for the conformational ‘sensitivity’ of the P–C stretching vibrations (Alk = C_2H_5 , $\text{iso-C}_3\text{H}_7$): the frequency of the vibrations $\nu[\text{P}–\text{C}(T)]$ is always lower than that of the vibrations $\nu[\text{P}–\text{C}(G)]$. The $\nu[\text{P}–\text{C}(G)]–\nu[\text{P}–\text{C}(T)]$ difference for compounds $\text{C}_2\text{H}_5\text{PX}_2$ (X = CH₃, Cl, F) varies between ~ 30 and 60 cm^{-1} . For the molecule **6**, this value decreases to $\sim 20\text{ cm}^{-1}$ and is only 7 cm^{-1} for ethylphosphine **4**, so that the doublet band corresponding to the vibrations $\nu(\text{P}–\text{C})$ can only be observed in the spectra of a solution of ethylphosphine **4** in liquid xenon.²⁰

The appearance of *gauche* and *trans* conformers in $n\text{-C}_3\text{H}_7\text{PX}_2$ is due to not only internal rotation about the P–C bond (the G and T conformers, respectively, see Fig. 2; Y = CH₂), but also the rotation with respect to the C–C bond (the g and t conformers, see Fig. 2). The t conformers are ~ 1.3 to 2.9 kJ mol^{-1} more energetically stable than the g conformers, the ΔH values decrease on going from the liquid to the gas phase or to solutions in liquid xenon. It is noteworthy that the enthalpy difference between the *gauche* and *trans* conformers of butane measured in the gas phase [$\sim 4.2\text{ kJ mol}^{-1}$ (see Ref. 156)] is much larger than the ΔH values for the corresponding n -propylphosphine conformers. Thus, substitution of a methyl group in the butane molecule by a bulky PX_2 group causes a decrease rather than an increase in the probability of the appearance of the *trans* conformers owing to internal rotation about the C–C bond.

The frequencies of the vibrations $\nu(\text{P}–\text{C})$ of propylphosphines are ‘sensitive’ to conformational transitions of both the $G \rightleftharpoons T$ and $g \rightleftharpoons t$ types. For $G \rightarrow T$ transition, the $\nu(\text{P}–\text{C})$ frequency decreases, as is the case of $\text{C}_2\text{H}_5\text{PX}_2$, whereas the $g \rightarrow t$ transition leads to an increase in this frequency. As a result, the highest-frequency IR absorption band (or Raman line) in the spectra of propylphosphines, corresponding to the vibrations $\nu(\text{P}–\text{C})$, is characteristic of the Gt conformers, while the frequencies of the peaks of the Tt conformers are $\sim 20–50\text{ cm}^{-1}$ lower and the peaks of the Gg and Tg conformers are even more shifted towards the low-frequency region (see Table 5). All these correlations between the changes in the frequency of the vibrations $\nu(\text{P}–\text{C})$ and the conformations of the ethylphosphino and propylphosphino groups are caused mainly by kinematic factors.

Orientations of alkyl groups (*gauche* and *trans*) with respect to the lone electron pair of the phosphorus atom are also characteristic of the molecules of the Alk_2PX or Alk_3P types. In the liquid or gas phase, the molecules of secondary and tertiary phosphines adopt usually several conformations, which is responsible for the appearance of multiplet IR absorption bands and Raman lines corresponding to the symmetrical and antisymmetrical stretching vibrations of the P–C bonds and to some other vibrations (see Table 5). However, all attempts to find general correlations between the molecular conformations and frequencies of any vibrations have failed.

3. Internal rotation of AlkOP fragments

The molecules of compounds with the general formula ROPX_2 can adopt either *trans* or *gauche* conformations, which is due to internal rotation about the P–O bond (see Fig. 1; X = CH₃, F, Cl; Y = O; Z = R). The *gauche* conformers are more favourable for X = CH₃, though a detectable amount of *trans* conformers is also present in the liquid phase. On the contrary, the *trans* conformers of alkyl phosphorodichloridites or alkyl phosphorodifluoridites are much more stable. According to the data of *ab initio* quantum-chemical calculations,^{91, 92} the energy difference between the G and T conformers for X = F is larger than for

X = Cl. In the former case, it is so large that the *G* conformer cannot be detected experimentally.^{91, 95–97}

No spectral indications of the existence of several conformers was observed for alkyl phosphorodichloridites ROPCl₂ (R = CH₃, C₂H₅) in the liquid or gas phase at room temperature.^{98–100, 103, 104} Based on the results of a gas-phase electron diffraction study¹⁰¹ and measurements of the dipole moments,⁹⁹ it was assumed that the molecule **3** adopts a nearly *gauche* conformation. However, a more detailed gas-phase electron diffraction study showed that this molecule adopts the *trans* conformation in the gas phase.¹⁰² Later, additional bands which cannot be attributed to the *trans* conformer were found in the spectra of glassy films of compound **3** and its solutions.¹⁰³ The high-frequency component of the doublet at 748/754 cm^{−1} corresponding to the vibrations $\nu_s(\text{POC})$ was attributed to the *gauche* conformer. The enthalpy difference between the *gauche* and *trans* conformers determined in CS₂ from the temperature dependence of the relative intensities of the bands at 748 and 754 cm^{−1} was found to be ~ 0.8 kJ mol^{−1} in favour of the latter. However, studies of methyl phosphorodichloridite **3** dissolved in liquid xenon revealed⁹² disappearance of some of the bands attributed to the *gauche* conformer.¹⁰³ Probably, these bands belong to molecular associates. However, the doublet band at 773/754 cm^{−1} corresponding to the stretching vibrations $\nu_s(\text{POC})$ retained in the solution in liquid xenon. It was suggested that this doublet is due to the Fermi resonance, since the relative intensities of the bands at 773 and 754 cm^{−1} were found to be temperature-independent.⁹²

It should be emphasised that the enthalpy differences between the *G* and *T* conformers of molecules AlkOPX₂ (X = CH₃, F, Cl) have not been measured as yet. The same is also true for the enthalpy differences between the *g* and *t* conformers, which are formed due to internal rotation about the O–C bond in this type of molecules (see Fig. 2, Y = O). These differences seem to be so large that only *t* conformers are observed in the liquid phase at room temperature.¹⁰⁴ This is also typical of the dialkyl ether molecules for which the *trans* conformers formed by internal rotation about the O–C bond are much more energetically favourable ($\Delta H \simeq 4.6\text{--}6.3$ kJ mol^{−1}).^{157–160} However, their *gauche* conformers are also present in detectable amounts both in the liquid and gas phase at room temperature.

Relative stabilities of the *gauche* and *trans* conformers change drastically upon introduction of the SCN group into the alkyl substituent of the ROPCl₂ molecules. The enthalpies of the *G* and *g* conformers of the molecule **35** become much lower than those of the *T* and *t* conformers, respectively.¹⁰⁵ The fact that the ‘twist’ conformers of the molecule **35** are more energetically favourable was attributed¹⁰⁵ to the effects of hypervalent intramolecular 1–5-attraction between the phosphorus and sulfur atoms. It should be noted that a doublet at 730 to ~ 715 cm^{−1} is observed in the spectra of liquid β -thiocyanatoethyl phosphorodichloridite **35** in the region characteristic of vibrations with predominant contribution of the $\nu_s(\text{POC})$ vibration and that the low-frequency line of the doublet disappears upon crystallisation.

Doublet IR absorption bands and Raman lines, assigned to the P–O stretching vibrations, are also observed in the spectra of liquid 2-chloro-1,3,2-oxathiaphospholane **37** (~ 760 to ~ 750 cm^{−1}), whose molecule can adopt several conformations owing to internal rotation about the P–O bond (see Fig. 3; conformers *a-E_C* and *e-E_C*, X = O, Y = S).¹⁰⁸ The *a-E_C* conformer, which is an analogue of the *T* conformers of acyclic alkoxy derivatives of the trivalent phosphorus compounds, was found to be ~ 2 kJ mol^{−1} more stable than the *e-E_C* conformer (an analogue of the *G* conformers).

Thus, despite some uncertainty in the data on the spectral indications of interconversions of the molecules containing one Alk–O–P group, one can say that they can be detected using the readily identifiable band corresponding to the POC stretching vibrations. However, the corresponding effects are weak and often remain unnoticed in the spectra of liquids measured at room

temperature. These effects can be observed if the spectral resolution is improved compared to that of the routine experiments. This can be attained in the low-temperature experiments. The kinematic effect of the *G* $\rightarrow$ *T* transition results in a decrease in the $\nu_s(\text{POC})$ frequency. However, for 2-chloro-1,3,2-oxathiaphospholane **37** an increase rather than a decrease in this frequency was observed, which is probably due to changes in the force field of the molecule in the course of interconversion of its conformers.

4. Internal rotation of AlkSP fragments

Alkyl phosphorodichloridothioites AlkSPCl₂ exist in the liquid and gas phases as mixtures of *T* and *G* conformers^{103, 128, 130–132} which are formed owing to internal rotation about the P–S bond (see Fig. 1; X = Cl, Y = S, Z = Alk). In the liquid phase, the *T* conformers are more energetically favourable^{130–132} (e.g., $\Delta H \sim 3.3$ kJ mol^{−1} for Alk = C₂H₅). Nevertheless, the amount of the *G* conformers at room temperature is comparable with that of the *T* conformers. For the molecule **28**, it is possible that great steric hindrances to the formation of the *trans* conformers (conformer A, see Section IV) lead to a decrease in their concentration in the equilibrium mixture. This can be assessed from the intensity ratio of the Raman lines corresponding to the vibrations $\nu(\text{P–S})$ of the *gauche* and *trans* conformers (see Table 25).

Rotation about the S–C bond can also be responsible for the formation of the *g* and *t* conformers (see Fig. 2; Y = S; Fig. 4, 5), the *trans* arrangement of the P–S and C–C bonds being more favourable for liquid alkyl phosphorodichloridothioites^{130–132} (e.g., $\Delta H_{g-t} \simeq 1.6$ kJ mol^{−1} for Alk = C₂H₅). For Alk = *n*-C₃H₇, the *g'* and *t'* conformers were also detected in the liquid phase¹³² which appear due to internal rotation about the C–C bond (see Fig. 4).

The molecules of alkyl phosphorodichloridothioites can adopt several conformations. A distinctive feature of their spectra is that the number of the IR absorption bands and Raman lines is much larger than one could expect. In particular, a complicated spectrum is observed in the region characteristic of the ‘co-operative’ stretching vibrations of the Cl₂PS fragment at $\sim 450\text{--}530$ cm^{−1}. The totally symmetric stretching vibration $\nu_s(\text{Cl}_2\text{PS})$ is ‘sensitive’ only to rotation about the P–S bond and the frequencies of this vibration for the *T* conformers are always lower than those of the *G* conformers ($\sim 495\text{--}505$ vs. $\sim 510\text{--}530$ cm^{−1}, respectively). A similar type of conformational ‘sensitivity’ was also observed for the frequencies of the vibrations $\nu(\text{P–S})$ of the molecule **28** (see Table 25). A decrease in the frequencies of vibrations with contribution of the P–S bond on going from the *G* to *T* conformers is mainly due to changes in the kinematic interactions in the molecule upon this transition.

The frequencies of the antisymmetric vibrations $\nu_{as}(\text{PCl}_2)$ of alkyl phosphorodichloridothioites depend on the conformations of the Cl₂PSC and PSCC fragments. The conformation in which the lone electron pair of the phosphorus atom lies in the plane of the PSCC fragment (the *Tt* conformation, see Figs 2 and 4; or the *Tg* conformation, see Fig. 5) is characterised by a frequency in the range between ~ 450 and 460 cm^{−1}. For all other conformations, the characteristic frequency $\nu_{as}(\text{PCl}_2)$ is observed at ≈ 490 to 495 cm^{−1} (see Table 25). The corresponding bands in the IR spectrum are masked by a very strong band corresponding to the antiphase stretching vibration of the P–S bond and PCl₂ fragment ($\sim 460\text{--}480$ cm^{−1}), which is conformationally ‘insensitive’. Because of this, the vibrations $\nu_{as}(\text{PCl}_2)$ of different conformers can be identified only in the Raman spectra in which they appear as depolarised shoulders on either side of a very strong polarised line at $\sim 460\text{--}480$ cm^{−1} corresponding to the above-mentioned antiphase stretching vibration of the P–S bond and PCl₂ group.

It is also convenient to use the Raman spectra for the attribution of the lines corresponding to the stretching vibrations S–C, the frequency of which depends on not only the structure of the alkyl radical at the sulfur atom, but also the conformation of the PSCC fragment. The conformer with *trans* arrangement of the P–S and C–C bonds (*t*, see Figs. 2 and 4; *g*, see Fig. 5) is

characterised by a higher frequency $\nu(\text{S}-\text{C})$ than the *gauche* conformer (*g*, see Figs. 2 and 4; *t*, see Fig. 5). Therefore, in the case of a mixture of the *g* and *t* conformers, the vibrations $\nu(\text{S}-\text{C})$ appear as doublets. For *S*-propyl phosphorodichlorodithioite, a triplet rather than a doublet corresponding to the vibrations $\nu(\text{S}-\text{C})$ is observed (see Table 25). This may be due to the fact that the frequency of this vibration depends on internal rotation about not only the $\text{S}-\text{C}$ bond, but also the $\text{C}-\text{C}$ bond. Nevertheless, the high-frequency components of the triplet correspond to the *t* conformation of the PSCC fragment.

The molecules of S,S',S'' -trialkyl phosphorotrithioites $(\text{AlkS})_3\text{P}$ are also characterised by the *G* and *T* orientations of the $\text{S}-\text{C}$ bonds with respect to the LEP of the phosphorus atom and either a *g* or *t* arrangement of the $\text{C}-\text{C}$ bonds with respect to the $\text{P}-\text{S}$ bonds. Usually, S,S',S'' -trialkyl phosphorotrithioites exist in the liquid or gas phase as mixtures of the *TGG* and/or *TGG'* conformers with the *GGG* conformers.^{130, 131, 161} The latter are less energetically favourable, but are present in considerable amounts at room temperature. Since the molecules of S,S',S'' -trialkyl phosphorotrithioites can adopt several conformations, some of the bands in their vibrational spectra become split into multiplets. However, only correlations between the conformations of the $\text{C}_2\text{H}_5\text{SP}$ fragments and the frequencies of the CH_2 rocking vibrations were found.^{130, 131} The *g* arrangement of the $\text{C}-\text{C}$ bond with respect to the $\text{P}-\text{S}$ bond corresponds to the $\nu(\text{CH}_2)$ frequency $\approx 780\text{ cm}^{-1}$, while the *t* arrangement corresponds to the $\nu(\text{CH}_2)$ frequency $\approx 760\text{ cm}^{-1}$. The same is also true for the molecule **45** (see Table 22).

X. Force constants of molecules containing trivalent phosphorus atoms

Among different classes of organophosphorus compounds, the force constants of alkylphosphines and their halogen-substituted derivatives have been studied in most detail. The potential fields of all these molecules share the common property that the effect of the phosphorus atom is confined to the distance to the α -C atom. For instance, the force constants of the CH_3 group of ethyl radical at the phosphorus atom remain virtually the same as in the ethane molecule. Because of this, only frequencies of the vibrations with predominant contribution of the $\text{P}-\text{C}$ bonds, and those of the methyl and methylene groups bound to the phosphorus atom are specific to alkylphosphines and, hence, can be regarded as having an analytical value.

On the other hand, variation of the alkyl radical in the AlkPX_2 molecules affects not only the force constants of the AlkP group, but also the parameters of the potential field of the PX_2 fragment. For instance, the force constants of the $\text{P}-\text{C}$ and $\text{P}-\text{X}$ bonds decrease simultaneously as the chain length of the alkyl radical increases.

Force constant	CH_3PF_2	$\text{C}_2\text{H}_5\text{PF}_2$	CH_3PCl_2	$\text{C}_2\text{H}_5\text{PCl}_2$
K_{PC}	2.76	2.54	2.94	2.65
K_{PF}	4.34	4.15		
K_{PCl}			2.08	1.94

For $\text{X} = \text{H}$, this dependence can be expressed quantitatively in the form of linear relationships (recall that the force constants are given in 10^2 N m^{-1})²²

$$K_{\text{PH}} = 0.126\sigma^* + 3.063,$$

$$K_{\text{PC}} = 0.235\sigma^* + 2.664,$$

where σ^* is the Taft constant of the alkyl group.¹⁶²

Introduction of halogens into the AlkP fragment leads to a pronounced decrease in the force constant K_{PC} and simultaneous increase in K_{PX} . For instance, the K_{PC} and K_{PCl} values respectively change from 2.94 and 2.08 for CH_3PCl_2 ⁵⁷ to 2.34 and 2.20 for $\text{ClCH}_2\text{PCl}_2$.⁶⁴

For the same alkyl radical, the force constant K_{PC} depends on the type of substituents X at the phosphorus atom; however, its

magnitude changes only slightly and does not obey simple rules. Thus for the CH_3PX_2 molecules the K_{PC} value increases from 2.66 to 2.94 on going from $\text{X} = \text{H}$,^{13, 14} to CH_3 ,^{13, 14, 43} F ⁵¹ and Cl .⁵⁷

The force constants of phosphorus-containing molecules can also be conformation dependent. For instance, the *gauche* $\rightarrow$ *trans* transition in the molecule **6** causes a decrease in the force constant K_{PH} from 3.05 to 3.01.²² Despite the small difference between these values, it was found to be reliable, since the $\text{P}-\text{H}$ stretching vibrations are known to be characteristic.²² Changes in the conformation of the polar ClCH_2P group has a more pronounced effect on the potential field of the molecule **15**: $K_{\text{PF}}(\text{gauche}) = 4.43$; $K_{\text{PF}}'(\text{gauche}) = 4.51$; $K_{\text{PF}}(\text{trans}) = 4.08$; $K_{\text{PC}}(\text{gauche}) = 2.81$; $K_{\text{PC}}(\text{trans}) = 2.84$; $K_{\text{CCl}}(\text{gauche}) = 3.09$; $K_{\text{CCl}}(\text{trans}) = 2.97$.

Thus, analysis of the force constants of the molecules of alkylphosphines and their halogen-substituted compounds suggests that the potential field of the phosphorus-containing fragment of the molecule strongly depends on the type and spatial orientation of each substituent at the phosphorus atom. On the other hand, the effect of the phosphorus-containing fragment on the force constants of adjacent groups is confined to the nearest environment of the phosphorus atom.

For phosphines with unsaturated groups at the phosphorus atom, the effect of the latter can likely extend to distances longer than the distance to the α -C atom. The force constants of the fragment $=\text{C}(\text{CH}_3)_2$ of molecules $\text{Cl}_2\text{PCH}=\text{C}(\text{CH}_3)_2$ (see Ref. 75) and $\text{CH}_2=\text{C}(\text{CH}_3)_2$ (see Ref. 160) differ appreciably, thus providing an explanation for the specific values of the characteristic vibrational frequencies of the alkenyl groups at the phosphorus atom. The potential fields of all these molecules share the common property that the force constants of the multiple carbon-carbon bonds at the trivalent phosphorus atom are smaller than those for the corresponding hydrocarbon molecules. The force constant $K_{\text{C}=\text{C}}$ for the molecules of alkenyl(dichloro)-phosphines is much smaller than those for ethylene and various alkenes and halogen-substituted alkenes [7.9 (Ref. 75) vs. 8.3–10.0 (Ref. 163), respectively]. On the other hand, the constants $K_{\text{PC}} \approx 3.1$ –3.5 (see Ref. 75) and $K_{\text{PCl}} \approx 2.3$ (see Ref. 75) are larger than the corresponding force constants of alkyl(dichloro)-phosphines [e.g., $K_{\text{PC}} = 2.94$ and $K_{\text{PCl}} = 2.08$ for the molecule **11** (see Ref. 57)].

A similar situation is also observed for the molecule **29**: the value of the constant $K_{\text{C}\equiv\text{C}} = 13.85$ (see Ref. 78) 'drops out' of the range between 14.22 and 15.62 (see Refs 164–167), which is characteristic of acetylene and its alkyl- and halogen-substituted derivatives; while the value of the constant $K_{\text{PC}} \approx 3.3$ (see Ref. 78) far exceeds the corresponding value [2.9 (see Ref. 43)] for the molecule **8**.

On the other hand, numerical values of the force constants K_{PC} and $K_{\text{C}\equiv\text{N}}$ for molecules **30** (see Ref. 79) and **31** (see Refs 84, 85) lie within the limits of conventional ranges, which are characteristic of trialkylphosphines and cyanogen halides.¹⁶⁷ Probably, this indicates that the phosphorus atom affects the electronic systems of adjacent $\text{C}\equiv\text{N}$ and $\text{C}\equiv\text{C}$ groups in a different manner.

For the AlkOP groups, this effect is most likely confined to the distance to the α -C atom of the ester group. In any case, the force constants of the ethyl fragments of molecules $\text{C}_2\text{H}_5\text{OPCl}_2$ (see Ref. 104) and $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ (see Ref. 168) are nearly equal. On the other hand, the force constant K_{PO} increases by about one unit on going from the ethyl to the methyl substituent.^{103, 104} Usually, variation of the nearest environment of the trivalent phosphorus atom has little effect on the force field of the AlkOP groups. For instance, $K_{\text{PO}} = 5.97$ and $K_{\text{OC}} = 4.91$ for CH_3OPCl_2 ,⁹² while for CH_3OPF_2 these values are $K_{\text{PO}} = 5.99$ and $K_{\text{OC}} = 4.51$.⁹¹

For the molecules of dialkylphosphoramides, the dependence of the force constant K_{PN} on the nature of substituents at the phosphorus atom is much more pronounced; for instance, the K_{PN} value increases from 4.5 to 5.1 on going from $(\text{CH}_3)_2\text{NPCl}_2$ to $(\text{CH}_3)_2\text{NPF}_2$.¹²⁵

Analysis of the force fields of the molecules of S-alkyl phosphorothioites shows that the phosphorus atom has no effect not only on the alkyl fragment of the molecule, but also on the force constant of the S—C bond. This seems to be reason why the spectral characteristics of the AlkS groups in the molecules of organophosphorus compounds coincide with the spectral indications of these groups in organosulfur compounds. Alkyl phosphorothioites are also characterised by the absence of pronounced effect of the alkyl radical on the force field of the phosphorus-containing fragment of the molecule. All acyclic compounds studied belonging to this class are characterised by the same force constant $K_{PS} = 2.0$.^{130–132} It should be noted that even passage to strained five-membered rings with endocyclic P—S bond¹⁰⁸ or replacement of the alkyl radical in the AlkSP group by the dimethoxythiophosphoryl fragment^{133, 134} decrease the K_{PS} value by only $\sim 10\%$.

As for the force fields of the molecules with the Si—P, Ge—P and P—P bonds, the corresponding data are too scarce to be used as a basis for any generalisation.

Closing the discussion of the force constants of the molecules of organophosphorus compounds, it should be emphasised that they can be used to predict the molecular spectra of related compounds for which studies by conventional methods of vibrational spectroscopy give no unambiguous solutions.¹⁶⁹ Additionally, rapid progress of computer industry opened the way to routine quantum-chemical calculations of the force constants. The first systematic studies of the so-called scaled 'quantum-chemical' potential fields of phosphines gave encouraging results.¹⁷⁰ Taken together, this allows one to hope that computer-assisted predictions of vibrational spectra of various organophosphorus compounds will become a routine procedure already in the near future.

XI. Conclusion

Trivalent tricoordinate phosphorus compounds contain no structural elements with such distinct spectral indications as, e.g., the phosphoryl group. However, analysis of the published data shows that the efficiency of vibrational spectroscopy in studying the structure of trivalent phosphorus compounds can be as high as in the case of pentavalent phosphorus compounds. This requires that the following salient features of the vibrational spectra of organophosphorus compounds be taken into account.

The effect of the phosphorus-containing fragment of the molecule is confined to the force constants of adjacent molecular fragments. This leads to a nearly complete additivity in that part of the spectral region which is due to the vibrations of more distant groups. For instance, the spectra of molecule $[(CH_3O)_2P(S)S]_3P$ nearly coincide with those of the corresponding *O,O'*-dimethyl phosphorodithioate $(CH_3O)_2P(S)SH$ (see Ref. 171) in the whole frequency range, except for the region corresponding to the stretching ($485\text{--}585\text{ cm}^{-1}$) and bending vibrations ($108\text{--}150$ and $350\text{--}405\text{ cm}^{-1}$) of the PSP fragments. Therefore, the spectrum of a phosphorus-containing molecule can be represented as the sum of the spectra of the fragments constituting the molecule minus the region corresponding to the vibrations of the nearest environment of the phosphorus atom. Therefore, the use of the data listed in Tables 1–25 can make the interpretation of vibrational spectra of trivalent phosphorus compounds much easier. For instance, spectral parameters of the C_2H_5OP fragment of an arbitrary molecule will coincide with the corresponding parameters of the *O*-ethyl fragment of ethyl phosphorodichloridite **34**. Vibrations of the POC fragment can appear to be an exception to this rule, since they can interact with vibrations of some other substituents through the shared phosphorus atom.

This example shows that consideration of the interactions between individual oscillators is of great importance to the analysis of the 'fingerprint' spectral regions. The data on the characteristic vibrations of different phosphorus-containing groups collected in this review will also help in predicting these

effects correctly. Stretching vibrations of the C—C bond in the C_2H_5P fragment of dichloro(ethyl)phosphine may serve as an example. This bond is connected to the PCl_2 group through the P—C valence bond. Nevertheless, no interaction between the vibration $\nu(C-C)$ and the vibrations of the PCl_2 group occurs (see Table 7). The reason is that the vibrational frequencies of the PCl_2 fragment are much lower than the frequency of the vibrations $\nu(C-C)$. A similar situation will be observed for any other molecules with heavy substituents at the phosphorus atom. Therefore, the frequencies of the vibrations $\nu(C-C)$ in the molecules **9**, **12** and **13** are equal. On the other hand, this frequency can vary on introduction of the C_2H_5P fragment into a molecule with light substituents at the phosphorus atom, since the character of the interaction between vibrations in the new molecule may be different. For instance, characteristic frequencies of the bending vibrations of the PH_2 group ($1073\text{--}1097\text{ cm}^{-1}$) are close to the frequency of the vibrations $\nu(C-C)$. Therefore, one can expect that in the molecule of ethylphosphine **4** these individual oscillators will interact, thus changing the frequency of the vibration $\nu(C-C)$ as compared to those of the same vibrations of molecules **9**, **12** and **13**. The data listed in Table 2 confirm this assumption.

Vibrations with contributions of the nearest environment of the phosphorus atom can change on going from one compound to another since the force constants of the phosphorus-containing molecular fragment depend on the types and conformations of all substituents at the phosphorus atom. Turning our attention to the above-mentioned example with the C_2H_5P fragment, one can say that the frequency of the stretching vibrations $\nu(P-C)$ will change from 636 cm^{-1} for ethylphosphine **4** to $631/663\text{ cm}^{-1}$ for the molecule **12** or to $655/682\text{ cm}^{-1}$ on going to ethyldifluorophosphine **13**.

Reliability of spectral–structural correlations for the 'fingerprint' region increases substantially, if the Raman spectra are used in combination with the IR spectra. For instance, several IR absorption bands in the region $550\text{--}710\text{ cm}^{-1}$ can indicate two or three P—C bonds in the molecule under study. However, if the molecules of compounds under study contain one P—C bond but can adopt several conformations, more than one IR absorption band will be observed in the above-mentioned spectral region. It is easy to discriminate between these two variants using the Raman spectrum. In the first case, an intense, strongly polarised Raman line will correspond to only one of the bands in the IR spectrum [see, e.g., $(CH_3)_2PCl$ or $(CH_3)_3P$ in Table 5], while the number of polarised lines in the Raman spectrum of the second compound will be equal to the number of peaks in the IR spectrum (e.g., $n-C_3H_7PCl_2$ or $n-C_3H_7PH_2$, see Table 5).

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^d — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*

Crown ethers in radiochemistry. Advances and prospects

S V Nesterov

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Abstract. Methods for the immobilisation of dicyclohexano- and non-substituted crown ethers are reviewed. Data on the radiation chemistry of these compounds and on the influence of irradiation on the properties of crown-containing extraction systems published over the last decade are discussed systematically. Examples of the use of crown ethers in different fields of radiochemistry are presented. The bibliography includes 199 references.

I. Introduction

Intense development of nuclear power resulted in the accumulation of huge volumes of liquid and solid radioactive waste, which present serious hazard to the environment.^{1,2} An approach to the reduction of the amount of radioactive wastes consists in upgrading of the existing technologies for the reprocessing of spent nuclear fuel as well as in the decrease in the bulk of waste subject to disposal and utilisation of the already available waste. The major procedure for the reprocessing of spent nuclear fuel is liquid extraction in which the transuranium elements are separated from fission fragments with subsequent regeneration of uranium and plutonium. Organophosphorus compounds used currently in extraction processes, such as tributyl phosphate, have a number of disadvantages, in particular low resistance to radiation and insufficient selectivity in binding radionuclides. In this context, the search for more efficient cation-binding compounds is topical.

Since the mid-1970s, macrocyclic polyethers or the so-called crown ethers have been regarded as promising extractants for the reprocessing of spent nuclear fuel and utilisation of radioactive wastes.³ Their feature is high selectivity of complexation with cations of metals possessing similar chemical properties; in many cases, the magnitude of the complex stability constant is characterised by the ratio of the size of the macrocycle cavity and the cation radius (see, *e.g.*, Refs 4 and 5). The existing methods for the synthesis of crown ethers allow preparation of ligands with the predetermined ability to bind cations of specific metals.⁶ Macrocyclic polyethers are chemically stable and can be easily regenerated. These properties of crown ethers stimulated studies on the

possibility of their use in the reprocessing of spent nuclear fuel, utilisation of radioactive waste in different stages of the nuclear fuel cycle and in radiochemical analysis. The most effective macrocyclic compounds for the separation of plutonium and uranium from fission fragments proved to be non-substituted and dicyclohexanocrown ethers. However, a substantial disadvantage of these extractants is their rather high solubility in water, which leads to their washout from the extraction and sorption systems.⁷ In this connection, studies are underway which are aimed at the development of methods for the synthesis of grafted and polymeric macrocyclic polyethers capable of binding selectively radionuclides and at the elaboration of novel technological processes based on them.

The present review discusses the methods for immobilisation and modification of non-substituted and dicyclohexanocrown ethers and synthesis of polymers based on them, generalises the published data on radiation chemistry of crown ethers and crown-containing extraction systems and presents examples of the use of macrocyclic polyethers in different fields of radiochemistry.

II. Methods for immobilisation of crown ethers

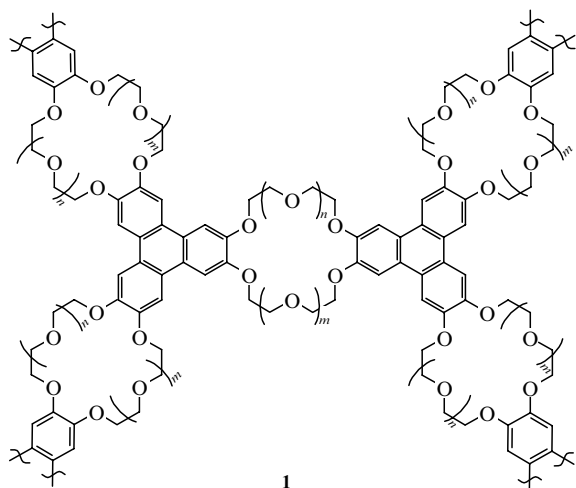
The efficiency of the use of crown ethers in extraction and sorption systems depends, among other factors, on the extent of losses associated with solubility of these compounds in an aqueous phase. The rather high solubility of crown ethers in water leads to the transfer of extractants from the organic to the aqueous phase, to transfer of water to the organic phase in extraction processes⁸ and the washout of complexants from the surface of porous supports in sorption processes.⁹ The necessity of an increase in hydrophobicity of non-substituted and dicyclohexanocrown ethers has been emphasised in the review by McDowell⁷ where he first considered in detail major problems to be solved for practical application of crown ethers in radiochemical technology. Appreciable progress has been achieved in the search for ways of decreasing the solubility of benzo- and azacrown ethers. The methods of immobilisation and synthesis of polymeric aza- and benzo-substituted crown ethers were considered in detail in a number of papers and monographs.^{10–15} A highly promising method for the synthesis of polymeric crown ethers, which can be used for the solution of radiochemical problems, is the anodic oxidation of dibenzocrown ethers on the surface of an electrode, which makes it possible to obtain crown-containing polymers of the type **I** in one step.^{16–19}

In the case of non-substituted and dicyclohexanocrown ethers, immobilisation and synthesis of polymeric compounds is much more difficult,²⁰ since these macrocycles are rather inert

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$n, m = 0-2$.

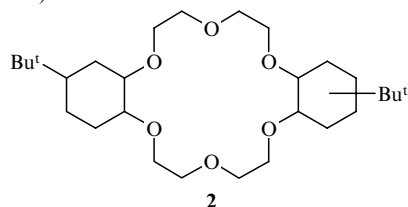
chemically. The basic methods for the reduction of their solubilities in water developed to date can be divided into several groups.

1. Synthesis of macrocyclic compounds with hydrophobic aliphatic substituents.

2. Synthesis of polymers containing fragments of non-substituted and cyclohexanocrown ethers or grafting of crown ethers onto porous supports.

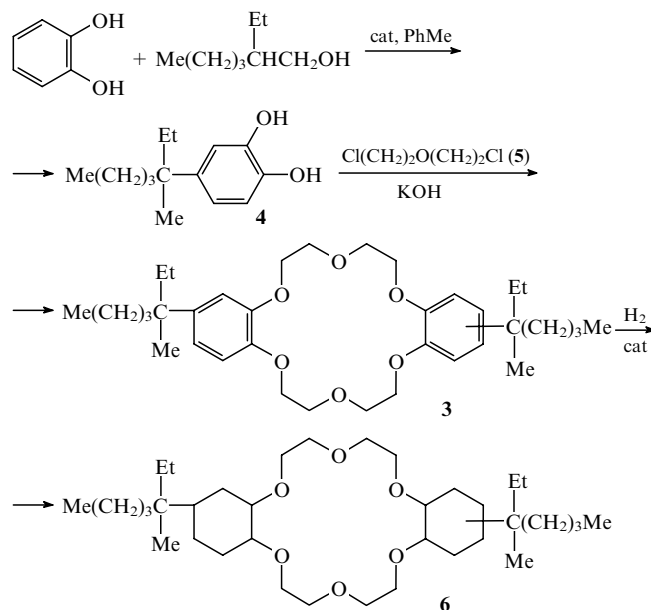
3. Immobilisation (without covalent binding) of crown ethers on a matrix which is inert with respect to metal cations or on the surface of a porous support.

The first group includes the methods of synthesis of dicyclohexanocrown ethers containing branched alkyl and/or other hydrophobic substituents. Introduction of branched alkyl chains into the cyclohexane ring leads to decrease in solubilities of crown ethers in water and simultaneously increases their solubilities in organic solvents. One of the most popular compounds of this type is 4',4'-(5')-di(*tert*-butylcyclohexano)-18-crown-6 (**2**, DTBDCH-18-C-6).^{21,22}



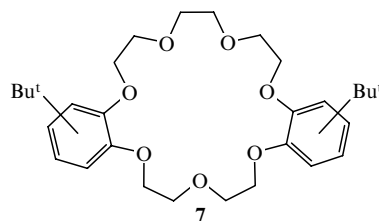
The crown ether **3** (DTODB-18-C-6) containing C₈ tertiary alkyl groups was obtained^{23,24} by cyclisation of alkylated pyrocatechol **4** with 2,2'-dichlorodiethyl ether (**5**, chlorex). Subsequent hydrogenation of dibenzocrown ether **3** leads to substituted dicyclohexanocrown ether **6** (DTODCH-18-C-6).

The crown ether **3** is soluble in all organic solvents (including alkanes) and is virtually insoluble in water and saline solutions. The solubility of the crown ether **6** in water proved to be close to that of ordinary dibenzocrown ethers. It is important that the introduction of *tert*-alkyl substituents did not change the ability

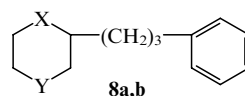


for complexation compared to that of non-substituted dicyclohexanocrown ethers.

McDowell *et al.*²⁵ described a method for the preparation of di-*tert*-butyldibenzo-21-crown-7 (**7**); its hydrogenation gives rise to the corresponding dicyclohexanocrown ether.

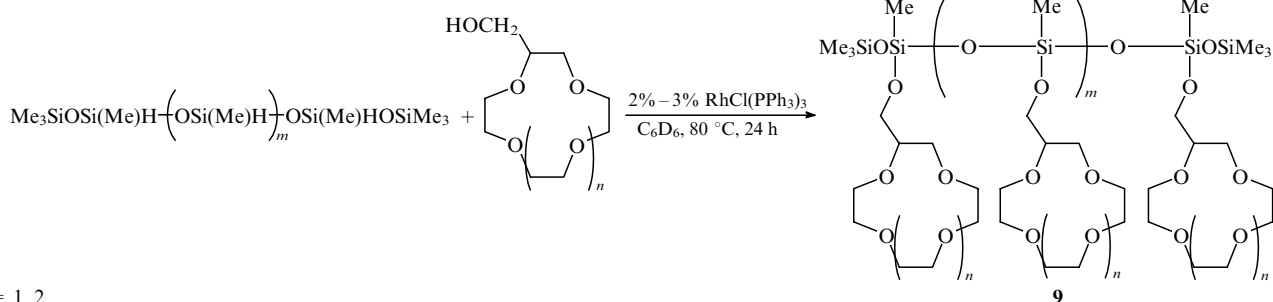


A promising method for the modification of non-substituted and cyclohexanocrown ethers was proposed.^{26,27} In the example of 1,4-dioxane and morpholine, which are low-molecular-weight analogues of crown ethers, the possibility of radical-chain addition of an aromatic hydrophobic group was demonstrated. Selective addition of allylbenzene to these cyclic ethers with the formation of compounds **8a,b** takes place upon γ -irradiation of a solution of allylbenzene (0.05–0.15 mol litre⁻¹) in 1,4-dioxane or morpholine. The degree of conversion of allylbenzene exceeds 30% at absorbed doses < 60 kGy.



X = Y = O (**a**), X = NH, Y = O (**b**).

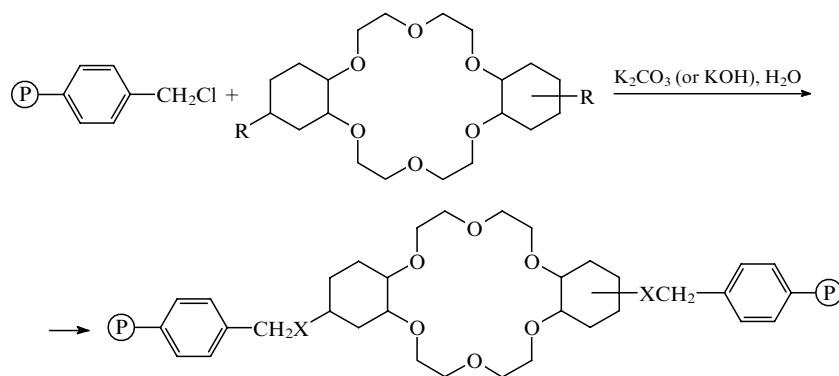
The second group includes methods of synthesis of polymeric crown ethers and methods of grafting of macrocycles on porous polymeric supports. Chauhan and Boudjouk²⁸ developed a one-



Scheme 1

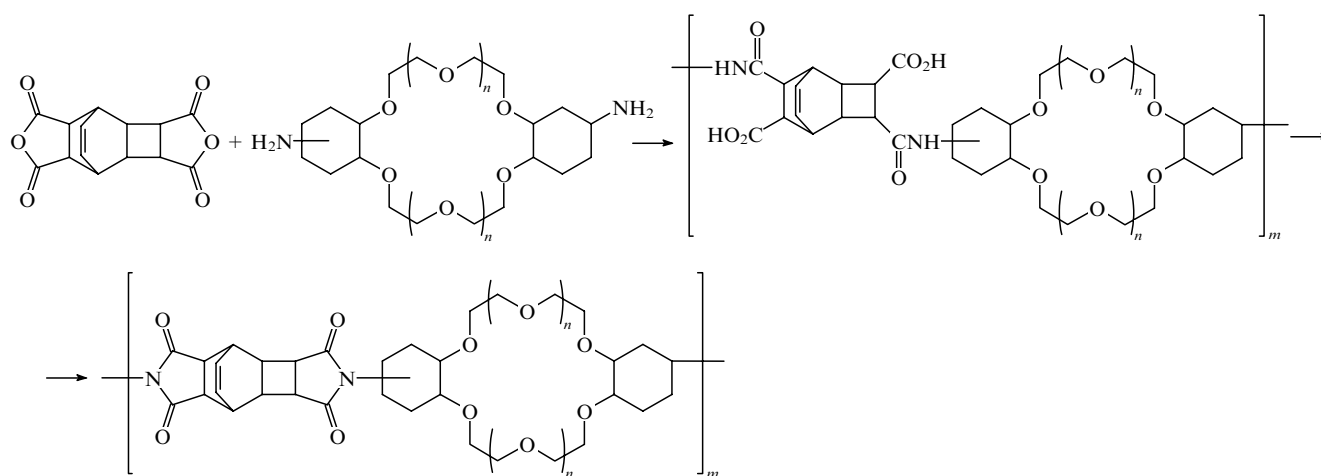
$n = 1, 2$.

Scheme 2



(P) is polymer; R = NH₂, CH(OH)Me, P(O)(OAlk)₂; X = NH, C(Me)O, P(O)OAlk.

Scheme 3



$n = 1$ (a), 2 (b).

10a,b

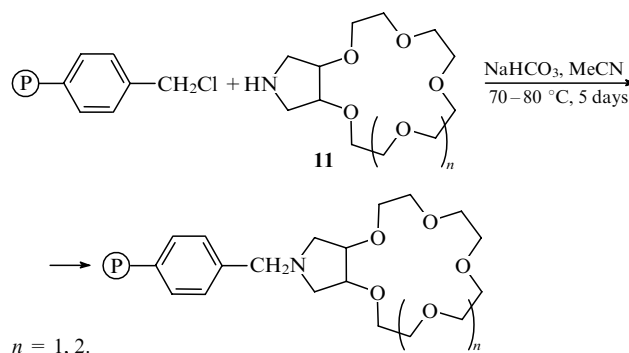
step method for the synthesis of polysiloxanes **9** containing fragments of non-substituted crown ethers and their oligomers. This method consists in selective catalytic oxidation of poly(methyl)siloxane and addition of 2-hydroxymethylcrown ether to the siloxane chain (Scheme 1).

The reaction proceeds under mild conditions, oxidation of Si–H bonds occurs without disproportionation and scission of the main chain. The polymers obtained are fairly well soluble in common organic solvents.

A method was proposed^{29–31} for immobilisation of a number of dicyclohexanocrown ethers on a support which is a chloromethylated copolymer of styrene with divinylbenzene (Scheme 2), the content of macrocyclic groups ranging from 0.75 to 1.6 mg-equiv g^{−1}. It is presumed that the groups X through which grafting is effected influence insignificantly the distribution of electron density in the crown-ether fragment. The electron-donor properties of the oxygen atoms are not weakened and the capacities for complexation of the grafted and free crown ethers differ insignificantly.

Kurmanaliev *et al.*³² described synthesis of polyimides **10a,b** containing the structural moiety of diaminodicyclohexano-18-crown-6 or diaminodicyclohexano-24-crown-8 and studied the transport of alkali metal cations through thin films of these polymers (Scheme 3). For polymer **10a**, the selectivity of the cation transport changes in the order K⁺ > Cs⁺ > Na⁺ and for polymer **10b** it changes in the order Cs⁺ > K⁺ > Na⁺. The sequences obtained match the binding capacities of free crown ethers.⁴ Thus, polymerisation of crown ethers does not change the selectivity of complexation.

Watanabe *et al.*³³ synthesised a novel crown ether **11** containing the pyrrolidine ring and grafted it onto a chloromethylated copolymer of styrene with divinylbenzene.



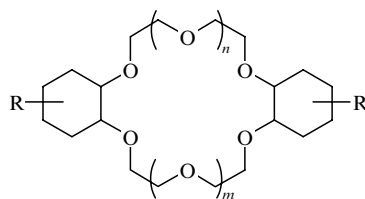
$n = 1, 2$.

A method of radical polymerisation in the presence of a larger-size crown ether, *viz.*, 42-crown-14, was employed to synthesise poly[(styrene)rotaxacrown ether] in which polymeric chains pass through the polyether rings.³⁴ Polyrotaxanes based on polyurathanes and dibenzo-24-crown-8 were obtained and their sorption properties with respect to a number of metals were studied.³⁵

The third group comprises methods for the preparation of compounds in which there are no covalent bonds between the crown ether molecules and the matrix. Solid extraction systems (SESys) and solid extraction solutions (SESol) synthesised by Yakshin *et al.*^{36–40} are characteristic representatives of crown-containing sorbents obtained by this method.

Solid extraction systems based on copolymers of styrene with divinylbenzene containing 40%–43% of a crown ether were obtained by adding a homogeneous mixture of styrene, divinylbenzene, crown ether and a polymerisation initiator to an aqueous solution of starch and subsequent polymerisation of the monomers.³⁶ This resulted in the formation of ball-shaped

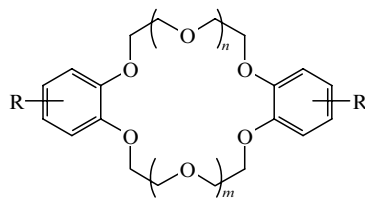
granules. Their stability was studied under conditions of contact with water for two days. The losses amounted to 90% for dicyclohexanocrown ethers such as dicyclohexano-18-crown-16 (DCH-18-C-6, **12**), DTBDCH-18-C-6 (**2**), dicyclohexano-21-crown-7 (DCH-21-C-7, **13**) and dicyclohexano-24-crown-8 (DCH-24-C-8, **14**).



2, 12–14

R = Bu^t, $n = m = 1$ (**2**); R = H: $n = m = 1$ (**12**), $n = 1, m = 2$ (**13**), $n = m = 2$ (**14**).

Washout of poorly water-soluble dibenzocrown ethers, *viz.*, dibenzo-18-crown-6 (**15**), dibenzo-21-crown-7 (**16**), dibenzo-24-crown-8 (**17**), dibenzo-30-crown-10 (**18**) and di(*tert*-butylbenzo)-18-crown-6 (**19**), occurred to lesser extent and the losses ranged from 10% to 30%. And finally, the losses of crown ethers



15–19

R = H: $n = m = 1$ (**15**), $n = 1, m = 2$ (**16**), $n = m = 2$ (**17**), $n = m = 3$ (**18**); R = Bu^t, $n = m = 1$ (**19**).

containing hydrophobic iso-octyl substituents in the aromatic and dicyclohexane rings, DTODB-18-C-6 (**3**) and DTODCH-18-C-6 (**4**), did not exceed 5%–10%.

In order to reduce losses of crown ethers, Yakshin *et al.*³⁶ proposed to presaturate the aqueous phase with the corresponding crown ether. Solid extraction solutions containing from 1% to 50% (w/w) of extractants were obtained^{37–39} by heating different liquid and low-melting crown ethers [DB-18-C-6 (**15**), *cis-syn-cis*-DCH-18-C-6 (**12**), DTBDCH-18-C-6 (**2**), DTODCH-18-C-6 (**4**) and others] with naphthalene, biphenyl or paraffin to their melting temperatures with subsequent dispersion of homogeneous melts in an aqueous solution of starch. The ball-shaped granules formed were separated and their sorption abilities were studied.

The onset of equilibrium in solutions in contact with SESys and SESol obtained by the methods described above takes a very long time (from 0.5 h to a few days^{38,40}) since under these conditions the binding of metal cations is limited by diffusion of ions (including anions) to the macrocyclic ligand through an inert matrix. For this reason, the use of these extractants under dynamic conditions is not advisable.

Solid extraction systems and solutions could not absorb metal cations from solutions in nitric acid. It was suggested that the macrocyclic centres are blocked in the nitric acid medium;^{40,41} however, the nature of this effect has not been clarified. It should be noted that such a block does not occur for solutions in hydrochloric acid.

The third group of methods includes also immobilisation of crown ethers on porous supports either by their application onto the surface or by impregnation. The advantage of the specimens obtained by this method is the accessibility of macrocyclic groups localised on the surface of the support for contact with metal ions.

Chuang and Lo⁴² described the preparation of a crown-containing sorbent by application of DCH-18-C-6 (**12**) onto silica gel. Silica gel was preliminarily dried at 110 °C, treated with dichlorodimethylsilane for substitution of free hydroxy groups

and then a solution of the crown ether in chloroform was added. After removal of the solvent, a sorbent was obtained which contained 3.8% of DCH-18-C-6 (**12**) and was sufficiently resistant to washout of the crown ether.

Horwitz *et al.*^{21,22,43,44} proposed a simple and efficient method for the preparation of a crown-containing sorbent which enables isolation of Sr²⁺ from nitric acid solutions. A solution of DTBDCH-18-C-6 (**2**) in octan-1-ol is immobilised on an inert porous support (Amberlite XAD-7 or Amberchrom CG-71 ms). The presence of hydrophobic *tert*-butyl substituents in the crown ether molecule provides good fixation of the macrocycle on the surface of the support on contact with aqueous solutions. This method for immobilisation of crown ethers has been patented; the commercial specimen called Sr-Spec may be purchased from the EICrom Industries Inc. (USA). Another impregnate was prepared at the V I Vernadsky Institute of Geochemistry (Russia) by impregnation of a porous copolymer of styrene and divinylbenzene with a 10% solution of DCH-18-C-6 (**12**) in chloroform or tetrachloroethane.^{2,45}

Nazarenko *et al.*⁴⁶ described a method of synthesis of crown-containing sorbents by coprecipitation of 18-crown-6 and phosphomolybdic heteropolyacid. These authors⁴⁶ also studied the influence of sorbent composition and medium acidity on the sorption properties with respect to rare-earth elements of the cerium group. The capacity of sorbents for the metal was 10–41 mg g^{−1} depending on the specimen composition and the nature of the metal to be sorbed. The data on the resistance of sorbents to washout are not presented.

III. Radiation-chemical transformations in extraction systems based on crown ethers

High resistance of an extractant to irradiation is one of the main factors which determine the efficiency of its use in radiochemical processes. It is presumed^{47,48} that the ionising irradiation initiates radiation-chemical transformations which may result in considerable changes in properties of the extraction system.

1. Decomposition of extractant leads to lower extraction efficiency.
2. The formation of radiolysis products affects unfavourably the selectivity of extraction.
3. The formation of active compounds prevents the partition of phases.
4. A third solid phase precipitates.
5. Formation of corrosive acids is possible.
6. Oligomers may be formed, which will unfavourably affect the extractant regeneration.

It is known⁴⁹ that macrocyclic polyethers form more stable complexes with metal cations in solutions than their non-cyclic analogues having the same number of donor atoms. This phenomenon was called the 'macrocyclic effect'. Upon irradiation of crown ethers, two main processes may occur, *viz.*, abstraction of a hydrogen atom from the methylene group of the polyether ring or from the hydrocarbon substituent (if present) and the cleavage of the ether bond of the macrocycle. The relationship between the extraction ability of a macrocycle and its cyclic structure was confirmed experimentally. Draye *et al.*^{50,51} synthesised products of the ether bond cleavage which can be formed from crown ethers upon irradiation. It turned out that the capacity for complexation of non-cyclic compounds mimicking the radiolysis products of DCH-18-C-6 (**12**) is much lower than that of the initial crown ether. Thus, the cleavage of the ether bond of the macrocycle upon radiolysis leads to a decrease in the efficiency of complexation.

The first studies of the radiation chemistry of macrocyclic polyethers were initiated in the 1980s.^{52–55} The major attention has been paid to the γ -radiolysis products of individual crown ethers in the gas and condensed phases.^{52–54,56} Radiation-chemical yields of molecular hydrogen [$G(\text{H}_2)$] and gaseous hydrocarbons have been calculated (Table 1). The yields obtained by different authors for the same compounds exhibited substantial

Table 1. Radiation-chemical yields of radicals [$G(R)$] and molecular hydrogen [$G(H_2)$] in γ -irradiated crown ethers.

Compound	$G(R) / n (100 \text{ eV})^{-1}$	Ref.	$G(H_2) / m (100 \text{ eV})^{-1}$	Ref.
1,4-Dioxane	2.7 ± 0.7	64	1.26	57
	—		1.41	56
Morpholine	5.3 ± 0.8	72	—	
12-Crown-4 (20a)	3.7 ± 0.7	64	—	
	5.4 ± 0.8	61	—	
15-Crown-5 (20b)	5.9 ± 0.7	64	1.60	56
	11.5 ± 2.0	61	—	
$\text{BeCl}_2 \cdot 15\text{-Crown-5}$	6.5 ± 0.8	66, 67	0.9 ± 0.2	58, 59
$\text{MgCl}_2 \cdot 15\text{-Crown-5}$	8.1 ± 1.1	66, 67	0.7 ± 0.2	58, 59
$\text{CaCl}_2 \cdot 15\text{-Crown-5}$	6.0 ± 1.1	66, 67	0.9 ± 0.2	58, 59
18-Crown-6 (20c)	5.7 ± 1.1	64	1.62	56
	3.2 ± 1.1	61	0.3	53
$\text{BeCl}_2 \cdot 18\text{-Crown-6}$	5.6 ± 0.8	67	0.7 ± 0.2	58, 59
$\text{MgCl}_2 \cdot 18\text{-Crown-6}$	7.9 ± 1.1	67	0.7 ± 0.1	58, 59
$\text{CaCl}_2 \cdot 18\text{-Crown-6}$	8.3 ± 0.7	67	1.0 ± 0.1	58, 59
$\text{SrCl}_2 \cdot 18\text{-Crown-6}$	9.3 ± 0.3	67	1.1 ± 0.2	58, 59
$\text{BaCl}_2 \cdot 18\text{-Crown-6}$	10.1 ± 0.5	67	—	
Dicyclohexano-18-crown-6 (12)	3.0	63	0.86	56
	—		0.12	53
Dicyclohexano-24-crown-8 (14)	2.9 ± 0.5	61	—	
Benzo-12-crown-4 (21a)	1.1 ± 0.2	70	—	
Benzo-15-crown-5 (21b)	0.7 ± 0.15	70	0.0014	54
Benzo-18-crown-6 (21c)	1.7 ± 0.3	70	—	
Dibenzo-18-crown-6 (15)	0.6 ± 0.1	70	0.175	56
	0.16 ± 0.02	61	0.01	53
	—		0.0017	54
3-Methyldibenzo-18-crown-6 (22a)	0.6 ± 0.1	70	—	
3,12-Dimethyldibenzo-18-crown-6 (22b)	1.0 ± 0.2	70	—	
3-Ethyldibenzo-18-crown-6 (22c)	1.0 ± 0.4	70	—	
3-Butyldibenzo-18-crown-6 (22d)	0.8 ± 0.1	70	—	
3,12-Dibutyldibenzo-18-crown-6 (22e)	1.2 ± 0.2	70	—	
3,12-Dihexyldibenzo-18-crown-6 (22f)	1.4 ± 0.3	70	—	
[4 : 6]-Dibenzo-30-crown-10 (22g)	0.7 ± 0.17	70	—	
Dibenzo-24-crown-8 (17)	1.3 ± 0.2	70	0.01	53
	—		0.0019	54
Dibenzo-30-crown-10 (18)	0.9 ± 0.15	70	—	
[2.1]-Cryptofix (23)	3.7 ± 0.7	72	—	
[2.2]-Cryptofix (24)	5.3 ± 0.8	72	—	
Hexathia-18-crown-6 (25)	1.1 ± 0.3	72	—	
[2.2.2]-Cryptand (26)	3.6 ± 0.6	72	—	

Note: n is the number of radicals, m is the number of molecules.

differences. Later, papers were published^{60, 61} in which intermediate species formed as a result of interaction of water radiolysis products with 18-C-6 and DCH-18-C-6 were studied by pulsed radiolysis and EPR methods. Based on the experimental results available at that time, it was concluded^{52–56, 60–62} that the abstraction of hydrogen atoms from the methylene groups of the polyether ring is predominant in the radiolysis.

Later, investigators began to give much attention to the identification of intermediate products of radiolysis of crown ethers. The results obtained provided evidence that it is the cleavage of the macrocycle that dominates in the radiolysis of crown ethers and extraction systems based on them.

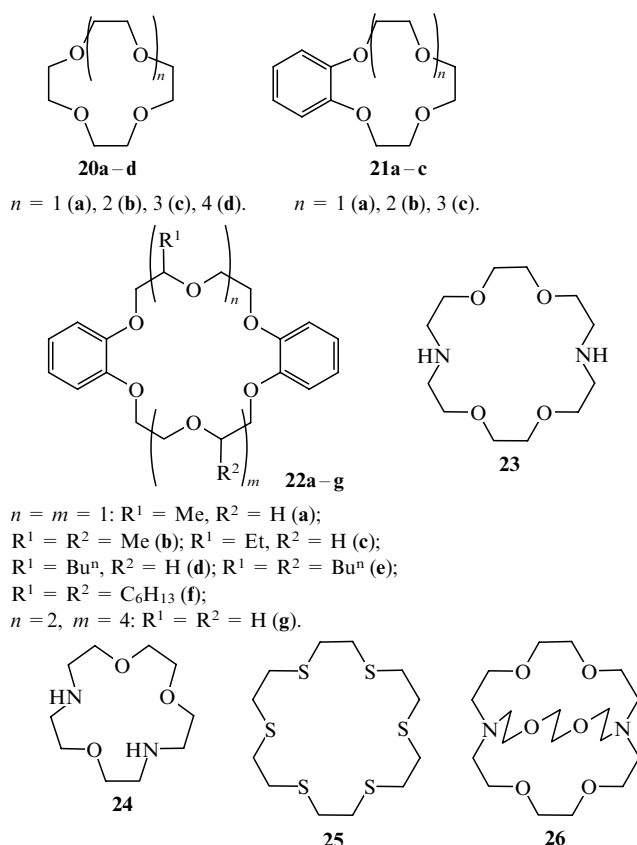
1. Radiolysis of crown ethers

Information about the nature of the intermediate and final radiolysis products of crown ethers, radiolysis mechanism and radiation-chemical yields is extremely important since this allows assessment of the macrocycle resistance to scission. Unfortunately, at present there are no data on primary radiolysis products (radical cations, excited molecules) or the contribution of ionisation and excitation processes to the mechanism of radiolysis of polyethers. Furthermore, there is no information that studies

along these lines are being carried out systematically. To some extent, this is explained by the complexity of experiments which require investigation of radiolysis of macrocyclic systems under conditions of matrix isolation of crown ethers or in adsorbed monolayers, *e.g.*, on zeolites. An exception are the studies of Kuruc *et al.*^{63, 64} who attempted to identify radicals and radical cations in γ -irradiated crown ethers by the methods of spin traps and isolation in Freon matrices. However, it was impossible to interpret unambiguously the results obtained because of poor resolution of the EPR spectra.

Much attention has been paid to studies of radical products of radiolysis of crown ethers stabilised at the temperature of liquid nitrogen. Schemes of the formation of radicals were proposed and assessment was made of the stability of γ -irradiated (at 77 K) non-substituted crown ethers **20a–d**,^{58, 59, 65} complexes of 15-crown-5 (**20b**) and 18-crown-6 (**20c**) with alkaline-earth metal chlorides,^{66–69} benzo- (**21a–c**) and dibenzocrown ethers (**22a–g**),^{58, 70, 71} aza- and thiocrown ethers (**23–25**), as well as of [2.2.2]-cryptand (**26**).^{72, 73}

It was proposed^{68, 71} to use the values of radiation chemical yields of radicals $G(R)$ as characteristics of the radiation stability (see Table 1). The data presented in Table 1 make it possible to



state that the radiation-chemical behaviour of crown ethers on the whole is similar to that of their low-molecular-weight non-cyclic analogues. Thus the yields of radicals $[G(R)]$ in non-substituted crown ethers are several times higher than those in thiocrown ethers. The same regularity was observed earlier in the radiolysis of aliphatic alcohols, ethers and thiols.⁷⁴ Benzo- and dibenzo-crown ethers show a negative deviation from the additivity rule in the formation of radicals, which is due to the transfer of absorbed energy from the macrocycle to the aromatic group, *i.e.*, a protection effect is observed. In addition, in benzocrown ethers the value of $G(R)$ depends on the size of the macrocycle, number of aromatic groups in the polyether ring and the length of the hydrocarbon chain of the alkyl substituent.⁷¹ The yields of radicals for complexes of non-substituted crown ethers with alkaline-earth metal chlorides are considerably higher than for 'free' polyethers. In this case, a substantial role is played by the matching of the macrocycle cavity size to the radius of the metal cation. Thus the resistance of 15-crown-5 complexes to radiation changes in the sequence $\text{Be}^{2+} \approx \text{Mg}^{2+} > \text{Ca}^{2+}$ (see Refs 67, 68), whereas for 18-crown-6 complexes the sequence is $\text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$ (see Ref. 68).

Apparently, the dominant process of radiolysis of the majority of crown ethers is the cleavage of the ether bond rather than the abstraction of a hydrogen atom, as was believed earlier.⁶² This conclusion is supported by the complexity and multicomponent pattern of the EPR spectra of γ -irradiated (at 77 K) crown ethers, which is explained^{59, 66, 69} by the superposition of signals belonging to several paramagnetic species and also by the absence of correlation between the radiation-chemical yields of radical products and of molecular hydrogen, $G(R) \neq 2G(\text{H}_2)$ (see Table 1).

An exception is hexathia-18-crown-6 where abstraction of hydrogen from the methylene groups of the polyether ring predominates.⁷³

2. Radiolysis of model extraction systems based on crown ethers

Investigation of the behaviour of extraction systems based on crown ethers under irradiation sheds light on the possibility of

their use under real conditions. Under the action of ionising radiation on an extraction system, both the processes of radiolysis of individual components of the system and the reactions of the products of solvent radiolysis (solvated electrons, hydrogen atoms and radicals) with the extractant contribute to the formation of products of radiation-chemical transformations. Due to these processes, the composition and properties of the system may be changed considerably. We will consider below the papers in which changes in the extraction capacity of crown-containing systems under the action of irradiation were studied and the stable products formed in the condensed phase were analysed.

Thus irradiation of DCH-18-C-6 (**12**) and 18-C-6 (**20c**) in chloroform solutions ($c = 0.05\text{--}0.1$ mol litre⁻¹) resulted in a 20% decrease in Sr^{2+} extraction from aqueous solutions of picric acid at absorbed doses of 30–50 kGy.⁷⁴ No new signals were present in the ¹H NMR spectra of irradiated solutions. This fact and the results of experiments in which preirradiated chloroform was used indicate that the coefficient of strontium distribution (D_{Sr} , *i.e.*, the ratio of the concentration of metal ions in the organic phase to that in the aqueous phase) decreases due to formation of chloroform radiolysis products, *viz.*, HCl and C_2Cl_6 . And indeed, the addition of these compounds to the extraction system led to a decrease in D_{Sr} .

Neither UV and IR spectra were changed nor new peaks in a chromatogram were observed following γ -irradiation of a 10% solution of DCH-18-C-6 (**12**) in chloroform to absorbed dose of 168 kGy.⁷⁵ Upon prolonged contact of DCH-18-C-6 with α -emitters (Pu^{4+} and U^{6+}) during which the total absorbed dose corresponded to 1.6 MGy, the extraction capacity of the macrocycle changed within acceptable limits: extraction of Pu^{4+} and U^{6+} decreased by $\sim 2\%$ and 23% , respectively. Irradiation of tributyl phosphate under analogous conditions leads to the formation of considerable amounts of mono- and dibutyl phosphate, due to which the selectivity of plutonium extraction in the process of plutonium and uranium extraction (PUREX) decreased considerably.

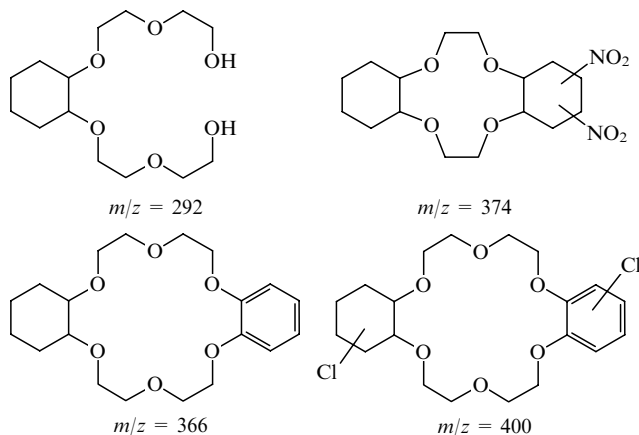
Shukla *et al.*⁷⁶ revealed a strong influence of irradiation on the ability of DCH-18-C-6 (**12**) solution in toluene (a mixture of isomers at a concentration ranging from 0.1 to 0.3 mol litre⁻¹) to extract Pu^{4+} and U^{6+} from solutions in nitric acid. Irradiation was carried out in the presence of air up to an absorbed dose of 710 kGy. The distribution coefficients of uranium and plutonium decreased two- and tenfold due to decomposition of the extractant and toluene.

At present, there is no unequivocal answer to the question about the influence of ionising irradiation on the properties of membranes based on crown ethers. On the one hand, preirradiation of a membrane based on 18-C-6 (**20c**) in chloroform ($c = 10^{-3}$ mol litre⁻¹) with a dose of 0.45 kGy in the presence of air results in a three- and twofold increase in the transport of Cs^+ and Sr^{2+} cations, respectively, (see Ref. 77) and the shift of selectivity of cation binding (from K^+ to Cs^+). Vijayavergiya and Mookerjee⁷⁷ explain this effect by the reaction of crown ether **20c** with chlorine atoms which are the radiolysis product of chloroform in the presence of HCl resulting from radiolysis of chloroform in air. These authors note the occurrence of a shift to the longwave region of the UV spectrum; however, they do not indicate to which absorption band this refers. On the other hand, the transport of U^{6+} and Pu^{4+} cations decreases after γ -irradiation of a membrane composed of a 0.2 M solution of DCH-18-C-6 in toluene on a polypropylene support.⁷⁶ The influence of irradiation becomes apparent after absorbed doses of 460 kGy for uranium and 100 kGy for plutonium. Above 710 kGy, the fluxes of U^{6+} and Pu^{4+} are decreased *ca.* twofold and *ca.* sixfold, respectively.

The radiation resistance of DCH-18-C-6 (**12**) immobilised on silica gel (3.8%) is estimated by comparing the sorption capacities of irradiated and non-irradiated samples with respect to Sr^{2+} (see Ref. 42). At absorbed doses ranging from 0 to 1.0 MGy, the sorption ability is virtually unchanged.

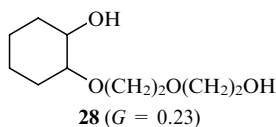
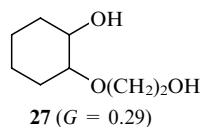
Analysis of the final radiolysis products of extraction systems based on crown ethers is a rather complicated task because of low radiation-chemical yields. Successful solution of this problem requires chromatographic separation of the decomposition products from the initial compounds. Thus irradiation (50–400 kGy) of B-15-C-5 (**21b**) in chloroform ($c = 0.001\text{--}0.15\text{ mol litre}^{-1}$) gave rise to the formation of the chloroform radiolysis products and mono- and dichloro derivatives of B-15-C-5 (**21b**) which represented ionic associated complexes $(\text{B-15-C-5})\text{H}^+\text{Cl}^-$ and $(\text{B-15-C-5})\text{H}^+\text{Cl}_2^-$. These were isolated chromatographically and identified by mass-spectrometry.⁷⁸ The products of the reaction of the chlorine atoms, which were derived from radiolysis of chloroform, with the aromatic ring of the crown ether were absent. The IR spectra of the radiolysis products revealed a band at 1740 cm^{-1} which was attributed to the carbonyl group. On this ground, a conclusion was made about the macrocycle opening.

Myasoedova and Dmitrieva⁷⁹ studied radiation-chemical transformations in a system containing $0.1\text{ mol litre}^{-1}$ of DCH-18-C-6 (**12**) in a 1 : 1 mixture of 1,1,2,2-tetrachloroethane and 3M HNO_3 . The organic and aqueous phases were stirred and irradiated in air. The absorbed dose was $\sim 10^5\text{ Gy}$ at a dose rate of 2 Gy s^{-1} . After distillation of tetrachloroethane, the residue was analysed by chromato-mass spectrometry. More than 40 radiolysis products were found. The probable products corresponding to the main peaks in the chromatogram are shown below:



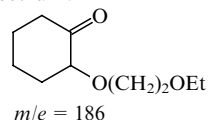
A scheme of radiation-chemical transformations of DCH-18-C-6 (**12**) was proposed. The major processes of radiolysis are presumed⁷⁹ to involve oxidation of the crown ether leading to the macrocycle opening and formation of acyclic products, addition of the products of tetrachloroethane and HNO_3 radiolysis to the initial crown ether, elimination of the oxyethylene fragment from the macrocycle with preservation of the cyclic structure (analogous to the fragmentation observed in the electron-impact mass spectrometry) and dehydrogenation of the cyclohexane ring. It was noted that at least two of the most abundant peaks in the chromatogram ($m/z\ 366$ and 400) were apparently due to the presence of an impurity derived from DB-18-C-6 and intermediate products appearing during its formation.

Draye *et al.*⁸⁰ studied the γ -radiolysis products of a solution of DCH-18-C-6 (**12**) and uranyl nitrate in 1M nitric acid using NMR and IR spectroscopy and chromato-mass spectrometry. Samples were irradiated without preliminary evacuation up to the absorbed dose of 3.29 MGy . New bands corresponding to the OH and C=O groups were observed in the IR spectra. At the same time, the NMR spectra of irradiated and non-irradiated samples remained identical. Of the seven basic peaks, the most prominent were the peaks with $m/z\ 160$ and 204 which are attributed to compounds **27** and **28**, respectively.



Unfortunately, Draye *et al.*⁸⁰ neither presented the experimental NMR and mass-spectra nor reported whether or not the samples were dehydrated before the analysis; therefore, the identification of the radiolysis products of crown ethers remains ambiguous.

Abashkin *et al.*⁴⁸ studied the radiolysis of *cis-syn-cis*- and *cis-anti-cis*-isomers of DCH-18-C-6 (**12**) and their complexes with strontium nitrate. At the absorbed doses below 500 kGy , no radiolysis products were found in free crown ether. Increase in the absorbed dose to 1500 kGy led to the appearance of a radiolysis product with a carbonyl group which was detected by chromatography. Presumably,⁴⁸ radiolysis resulted in a symmetrical scission of the macrocycle over two C–O bonds with the formation of a compound giving a peak at $m/z\ 186$ in the mass spectrum.



It was found that *cis-syn-cis*-**12** is more stable than *cis-anti-cis*-**12**. The complex of DCH-18-C-6 (**12**) with strontium nitrate is less resistant to the radiation than the free crown ether. At 500 kGy , complex decomposition products are formed, which is evidenced by the appearance of the absorption bands of the unbound nitrate in the IR spectrum and by the decrease in the intensity of the absorption bands of the complex. The macrocycle of the complex also undergoes decomposition yielding a product containing a carbonyl group.

Thus, DCH-18-C-6 possesses high resistance to irradiation in the range of doses received by extractants during the spent nuclear fuel reprocessing cycle, and decomposition of the macrocycle may be disregarded. Irradiation of extraction systems based on crown ethers with larger doses leads mainly to macrocycle scission, while the formation of cross-linking or polymerisation products is hardly probable. A decrease in the extraction ability of the systems based on crown ethers under the action of ionising irradiation is associated with the formation of the solvent radiolysis products; for this reason, the use of chlorine-containing solvents is undesirable.

In studies of the radiolysis of dicyclohexanocrown ethers and their complexes with metal cations, the purity of samples is highly important, since even insignificant amounts of dibenzocrown ethers may lead to erroneous identification of the radiolysis products.^{48,79}

IV. Areas of application of crown ethers

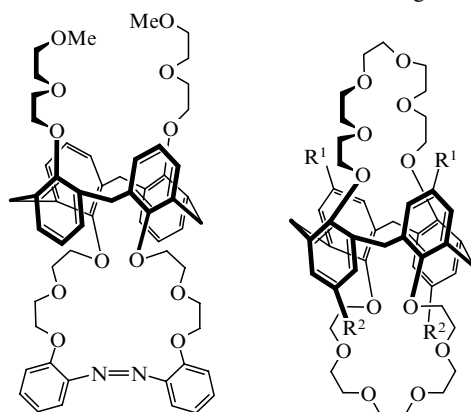
1. Reprocessing of spent nuclear fuel and extraction of fission fragments from radioactive waste

Reprocessing of spent nuclear fuel is a stage of the fuel cycle in which uranium and plutonium are separated from fission fragments. The major role in this process is played by liquid extraction. The use of crown ethers as extractants, in particular of dicyclohexanocrown ethers, ensures higher selectivity of the extraction of uranium and transuranium elements compared to that provided by extractants used currently and allows separation of these radionuclides from the fission fragments.^{3,8} New extraction processes based on the use of macrocyclic polyethers were proposed which allow selective isolation of Sr and Tc,^{81–85} U(VI) and Pu(IV)^{51,86} from solutions in nitric acid with high specific activity.

Dicyclohexanocrown ethers are efficient in the utilisation of liquid radioactive waste formed in the processing of nuclear fuel and deactivation of equipment. Depending on their origin, the radioactive wastes can have acidic or alkaline reaction. Concentrates of such wastes possess high activities due to the presence of long-living cesium and strontium isotopes with half-life times ($\tau_{1/2}$) of 28.5 and 30.1 years for ^{90}Sr and ^{137}Cs , respectively.⁸⁷ These concentrates are stored in geological storage pits. Selective extraction of radionuclides from them makes it possible to decrease considerably the bulk of waste, which simplifies further reprocessing and storage. In addition, ^{90}Sr and ^{137}Cs are widely used as

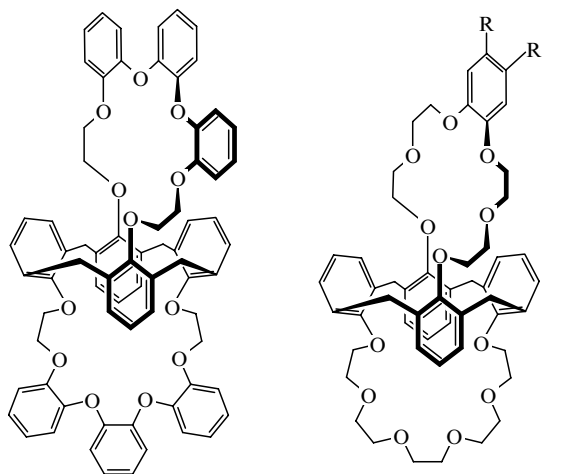
sources of β -radiation and energy generators.⁸⁸ At present, two processes of radioactive waste treatment are under testing in the USA. Thus in the Argonne National Laboratory, a process for selective extraction of ^{90}Sr (the so-called SREX, *i.e.*, Strontium Extraction) from solutions in nitric acid was developed. This method employs DTBDCH-18-C-6 (**2**) ($c = 0.15 \text{ mol litre}^{-1}$) as a selective extractant of Sr^{2+} . The extraction system is supplemented with tributyl phosphate to prevent formation of a third phase and with kerosene Isopar L[®] as the solvent. Pilot technological testing has shown that crown ether **2** allows 99.98% extraction of strontium in a single cycle, the extract containing virtually no Na, Fe, Ca ions and other ballast elements.^{84,85} A disadvantage of the SREX process is co-extraction of Pb^{2+} and K^+ cations, and this fact requires that the process included an additional stage for the separation of these cations. Researchers of the Oak Ridge National Laboratory devised an SRTALK process for the extraction of technetium and strontium from alkaline radioactive waste.^{81–83} The extraction system consists of DTBDCH-18-C-6 (**2**) solution ($c = 0.02 \text{ mol litre}^{-1}$) in a 1 : 1 (v/v) mixture of kerosene Isopar L[®] and tributyl phosphate as a modifier.

Selective ligands with respect to cesium cations are dibenzo-crown ethers and calixarenes containing fragments of crown ethers. At present, intensive studies of extraction and sorption systems based on them and aimed at extracting Cs from radioactive waste are underway.^{89–94} Photosensitive monocrown-6-azobenzocalix[4]arene (**29**) was synthesised.^{89,95} When it is used for the extraction of Cs^+ ions, the distribution coefficient increases threefold under the action of UV light.



29
 $\text{R}^1 = \text{COOH}$, $\text{R}^2 = \text{H}$ (a); $\text{R}^1 = \text{R}^2 = \text{SO}_3\text{Na}$ (b);
 $\text{R}^1 = \text{R}^2 = \text{SO}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$ (c).

The preparation of water-soluble calix[4]arene-bis(crown ethers) **30a–c** has been described. These compounds were shown⁹¹ to have high affinities for cesium ions. Calix[4]arene[



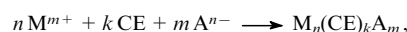
31
32, 33 $\text{R} = \text{H}$ (**32**);
 $\text{R}_2 = \text{CH}=\text{CHCH}=\text{CH}$ (**33**).

bis(tribenzo)-crown-6] (**31**)⁹⁰ and non-symmetrical calix[4]arene[bis-crown ethers] (**32, 33**)⁹⁶ were synthesised. These were shown to possess high cation-binding abilities for cesium ions and to be virtually inert with respect to sodium ions. High selectivities of compounds **31–33** are determined by the presence of aromatic substituents in the polyether ring resulting in a change in the sp^3 hybridisation of carbon atoms of the oxyethylene moiety to sp^2 hybridisation.⁹⁰

It was proposed to use crown-containing calixarenes as supports in membranes for selective extraction of cesium ions from nuclear waste^{97–99} and in ion-selective electrodes.¹⁰⁰ Lamare *et al.*¹⁰¹ described a method for selective extraction of traces of cesium by calixarene-crown ethers from sodium nitrate solutions.

a. Effect of solution acidity and the crown ether structure on the extraction efficiency

Quantitative parameters of the extraction process are characterised by the distribution coefficient D and the extraction constant K_{ex} . As a rule, extraction of metal ions by a macrocycle from acidic and neutral solutions is described^{102–107} by the scheme



where M is the metal cation, m is the metal oxidation state, CE is a crown ether, k is the number of macrocyclic molecules involved in complexation, A is an anion and n is the anion charge. $\text{M}_n(\text{CE})_k\text{A}_m$ is the complex of the crown ether with the cation.

For most systems, $k = 1$ or 2 . For $k = 2$, a sandwich-like complex is formed.

The extraction constant may be calculated using the following relation:

$$K_{\text{ex}} = \frac{[\text{M}_n(\text{CE})_k\text{A}_m]^*}{[\text{M}^{m+}]^n [\text{CE}]^k [\text{A}^{n-}]^m}, \quad (1)$$

where $[\text{CE}]$ and $[\text{M}_n(\text{CE})_k\text{A}_m]^*$ are the concentrations of a crown ether and its complex in the organic phase, $[\text{M}^{m+}]$ and $[\text{A}^{n-}]$ are the concentrations of a cation and an anion in the aqueous phase.

The distribution coefficient is determined from the relation

$$D = \frac{[\text{M}_n(\text{CE})_k\text{A}_m]^*}{[\text{M}^{m+}]^n}. \quad (2)$$

Substituting K_{ex} from the relation (1) gives

$$D = K_{\text{ex}}[\text{CE}]^k [\text{A}^{n-}]^m \quad (3)$$

or

$$\log D = \log K_{\text{ex}} + k \log [\text{CE}] + m \log [\text{A}^{n-}]. \quad (4)$$

The compositions of crown-containing extraction systems and the distribution coefficients of Cs, Sr, U and Pu ions obtained for them are listed in Table 2.

The dependence of the distribution coefficient of a metal on the concentration of crown ether at a constant concentration of a counterion allows determination of the extraction constant and the composition of the crown ether complexes with metal cations (Table 3).

It should be noted that the above-cited scheme of extraction of metal ions by macrocycles does not take into account a number of factors. As a rule, transition of a metal salt into the organic phase in the absence of a macrocycle and dissociation of a macrocyclic complex in the organic phase may be disregarded,¹¹³ however, the solution acidity is one of the crucial factors determining quantitative parameters and the mechanism of the extraction process. In an acidic solution, complexation is complicated by the involvement of protonated ligands.^{119, 122, 123} In addition, it was found that DCH-18-C-6 (**12**) forms complexes effectively with nitric and picric acids. It is noteworthy that up to 10 molecules of nitric acid per macrocycle can be extracted from the aqueous to the organic phase.^{3, 8, 124, 125} The effect of concentration of nitric and picric acids on the extraction of strontium,^{87, 102–104, 119} uranium,^{105, 107, 114, 126, 127} and plutonium^{8, 105, 106, 120} by dicyclohexanocrown ethers was investigated in numerous studies. It was

Table 2. Distribution coefficients of Cs, Sr, U and Pu ions in extraction systems based on crown ethers.

Crown ether	Concentration of crown ether /mol litre ⁻¹	Solvent	Cation	Acid	Concentration /mol litre ⁻¹	<i>D</i>	Ref.
DCH-18-C-6 (12)	0.1	chloroform	Sr ²⁺	HNO ₃ ^a	2	720	108
	0.1	n-hexylbenzene	Sr ²⁺	HNO ₃	1	2.66	109
	0.1	<i>o</i> -nitrophenyloctyl ether	Sr ²⁺	HNO ₃	1	1.58	109
	0.1	n-octanol	Sr ²⁺	HNO ₃	4.05	3.31	102
	0.1	1,1,2,2-tetrachloroethane	Sr ²⁺	HNO ₃	3	7.8	110
see ^b	0.05	"	Sr ²⁺	HNO ₃	1.5	24.4	111
see ^b	0.05	1,2-dichloroethane	Sr ²⁺	HNO ₃	2.0	8.7	111
see ^b	0.05	nitrobenzene	Sr ²⁺	HNO ₃	2.0	2.6	111
see ^b	0.05	chloroform	Sr ²⁺	HNO ₃	3.0	24.9	111
see ^c	0.014	1,1,2,2-tetrachloroethane	Sr ²⁺	HNO ₃	1.0	8.7	87
see ^c	0.05	chloroform	Sr ²⁺	picric acid	0.01	1000	47
see ^b	0.1	"	Sr ²⁺	HNO ₃	3.0	62.3	112
see ^b	0.1	nitrobenzene	Sr ²⁺	HNO ₃	3.0	45.7	112
see ^c	0.2	toluene	Pu ⁴⁺	HNO ₃	3.0	64.28	105
see ^c	0.2	benzonitrile	Pu ⁴⁺	HNO ₃	3.0	48.41	105
see ^c	0.2	<i>o</i> -dichlorobenzene	Pu ⁴⁺	HNO ₃	3.0	18.04	105
see ^c	0.2	dichloromethane	Pu ⁴⁺	HNO ₃	3.0	17.93	105
see ^c	0.2	1,2-dichloroethane	Pu ⁴⁺	HNO ₃	3.0	17.78	105
see ^c	0.2	benzene	Pu ⁴⁺	HNO ₃	3.0	14.84	105
see ^c	0.2	chloroform	Pu ⁴⁺	HNO ₃	3.0	6.92	105
see ^c	0.2	xylene	Pu ⁴⁺	HNO ₃	3.0	0.72	105
see ^c	0.1	toluene	Pu ⁴⁺	HNO ₃	5.0	13	106
see ^c	0.1	1,2-dichloroethane	Pu ⁴⁺	HNO ₃	4.0	> 10	8
see ^c	0.1	benzene	U ⁶⁺	picric acid	0.04	0.142	113
see ^c	0.1	1,2-dichloroethane	U ⁶⁺	"	0.04	0.237	113
see ^b	0.1	chloroform	U ⁶⁺	HNO ₃	5.0	1.27	114
see ^b	0.2	toluene	U ⁶⁺	HNO ₃	7.2	0.52	107
see ^b	0.537	benzonitrile	Pu ⁴⁺	HNO ₃	4.5	98	86
see ^b	0.537	"	U ⁶⁺	HNO ₃	4.5	5.6	86
DTBDCH-18-C-6 (2)	0.1	n-octanol	Sr ²⁺	HNO ₃	4.05	15.8	102
	0.1	n-hexylbenzene	Sr ²⁺	HNO ₃	1	1.99	109
	0.1	<i>o</i> -nitrophenyloctyl ether	Sr ²⁺	HNO ₃	1	0.25	109
18-C-6 (20c)	0.1	1,2-dichloroethane	Pu ⁴⁺	HNO ₃	8.0	~ 10	8
	0.1	benzene	U ⁶⁺	picric acid	0.04	0.028	113
	0.1	1,2-dichloroethane	U ⁶⁺	"	0.04	0.533	113
	0.11	chloroform	U ⁶⁺	picric acid ^d		0.092	115
	0.1	"	U ⁶⁺	HNO ₃	7.0	0.16	114
	0.15	"	Sr ²⁺	HNO ₃	10.0	0.63	103
DB-21-C-7 (16)	0.1	"	Sr ²⁺	HNO ₃	2.0	0.035	112
B-15-C-5 (21b)	0.11	"	U ⁶⁺	picric acid ^d		0.116	115
DCH-24-C-8 (14)	0.1	"	U ⁶⁺	HNO ₃	7.0	1.62	114
4-Methylbenzo-15-crown-5	0.1	benzene	U ⁶⁺	picric acid	0.04	0.204	113
	0.1	1,2-dichloroethane	U ⁶⁺	"	0.04	0.146	113
<i>tert</i> -Butylbenzo-21-crown-7 or n-decylbenzo-21-crown-7	0.1	n-hexylbenzene	Cs ⁺	HNO ₃	1	0.1	116
DB-21-C-7	0.025	1,2-dichloroethane	Cs ⁺	see ^e		9 × 10 ⁻³	117
Tribenzo-21-crown-7	0.025	"	Cs ⁺	see ^e		2 × 10 ⁻³	117
DB-24-C-8	0.025	"	Cs ⁺	see ^e		3 × 10 ⁻³	117
Tribenzo-24-crown-8	0.025	"	Cs ⁺	see ^e		6 × 10 ⁻³	117
Tetrabenzo-24-crown-8	0.025	"	Cs ⁺	see ^e		2 × 10 ⁻²	117
DB-24-C-8 (17)	0.01	chloroform	Cs ⁺	picric acid	0.01	∞	118
	0.01	dichloromethane	Cs ⁺	"	0.01	∞	118
	0.01	1,2-dichloroethane	Cs ⁺	"	0.01	∞	118
	0.01	nitrobenzene	Cs ⁺	"	0.01	∞	118
Di(<i>tert</i> -butylbenzo)-21-crown-7	0.01	<i>o</i> -xylene	Cs ⁺	see ^f		2.17 × 10 ⁻⁴	93
	0.01	1,2-dichlorobenzene	Cs ⁺	see ^f		1.12 × 10 ⁻³	93
	0.01	1,2-dichloroethane	Cs ⁺	see ^f		4.62 × 10 ⁻³	93
	0.01	nitrobenzene	Cs ⁺	see ^f		1.64 × 10 ⁻²	93

^a 5M HCl was added; ^b *cis-syn-cis*-isomer, ^c mixture of isomers, ^d pH = 3, ^e neutral medium, ^f alkaline medium, [OH⁻] = 1.75 g-ion litre⁻¹.

found that the efficiency of the extraction depends on the nature of the solvent, metal, counterion, *etc.* Thus in the extraction of Sr²⁺ by DCH-18-C-6 (**12**) in a butanol–octanol mixture (80:20), the distribution coefficient *D*_{Sr} depends on the concentration of nitric

acid and increases as the HNO₃ concentration is increased from 1 to 8 mol litre⁻¹ (see Ref. 102). When 1,1,2,2-tetrachloroethane⁸⁷ and chloroform¹¹¹ are used as solvents, the distribution coefficient of Sr²⁺ reaches maxima for HNO₃ concentrations of

Table 3. Composition of complexes of crown ethers with metal cations.

Cation	Crown ether	Ratio of components in the complex	Ref.
Sr ²⁺	18-C-6 (20c)	1 : 1	103
	DCH-18-C-6 (12)	1 : 2	102, 119
Pu ⁴⁺	DCH-18-C-6 (12)	1 : 2	3, 105, 120
U ⁴⁺	15-C-5 (20b)	1 : 3	121
	B-15-C-5 (21b)	1 : 2	114
	18-C-6 (20c)	1 : 1	114
	DCH-18-C-6 (12)	1 : 1	105

1.25 and 3.0 mol litre⁻¹, respectively. For the U⁶⁺ ion, the D_U increases as the concentration of HNO₃ is increased and reaches a plateau for its concentration of 5–8 mol litre⁻¹ (Refs 105, 114). The dependence of D_{Pu} on solution acidity has a maximum which is shifted from 4–5 to 3–4 mol litre⁻¹ HNO₃ as the macrocycle concentration is increased from 0.05 to 0.2 mol litre⁻¹ (see Refs 105, 120). Presumably,^{8,105} the initial enhancement of the Pu(IV) extraction is due to salting out of the metal by nitric acid. Subsequent decrease in D_{Pu} as the acidity is increased was explained by the displacement of the metal from the organic phase due to the reaction of the ligand with the acid.⁸ However, an alternative explanation was also proposed:¹⁰⁵ this effect is believed to be related to the formation of less extractable acidic complexes of the type HPU(NO₃)₅ and H₂Pu₄(NO₃)₆.

The structure of crown ether, in particular the size of the polyether ring and the nature of the substituent, exert a strong effect on the efficiency of extraction. Relevant studies were devoted to the investigation of the influence of the crown ether structure on the extraction of cesium,^{118, 128–130} strontium,^{47, 87, 103} uranium and plutonium^{8, 105, 131} and other actinides.⁸ In the extraction of ions of alkali and alkali-earth metals, crown ethers behave in conformity with the concept of geometric correspondence of the size of the cation to the size of the polyether ring cavity. Thus the optimum macrocycles for the binding of strontium are 18-C-6 (**20c**) and DCH-18-C-6 (**12**), whereas dicyclohexano- and dibenzo-21-crown-7 and -24-crown-8 are selective ligands for cesium cations.^{132, 133} The effect of the macrocycle size on the extractability of uranium and plutonium ions is of a more complex character. The extraction ability of crown ethers in toluene¹⁰⁵ or chloroform¹¹⁴ in regard of UO₂(NO₃)₂ and Pu(NO₃)₄ in a nitric acid medium proved to be changed in parallel with the macrocycle size and had the following order: DCH-18-C-6 (**12**) > DB-24-C-8 (**17**) > DB-18-C-6 (**15**) > B-15-C-5 (**21b**).

However, these sequences for U⁶⁺ and Pu⁴⁺ ions do not coincide in the case of extraction with solutions of crown ethers in dichloroethane from nitric acid media. The extractability of U⁶⁺ decreases in the order: DCH-18-C-6 (**12**) > DCH-24-C-8 (**14**) > DB-24-C-8 (**17**) > DB-18-C-6 (**15**) > 15-C-5 (**20b**) > 18-C-6 (**20c**), while that of Pu⁴⁺ decreases in the order: DCH-24-C-8 (**14**) ≈ DCH-18-C-6 (**12**) > 15-C-5 (**20b**) > 18-C-6 (**20c**) > DB-24-C-8 (**17**) > DB-18-C-6 (**15**).³

In the extraction of uranyl ions from solutions in picric acid, the increase in the size of the macrocycle cavity leads to a decrease in $D_{UO_2^{2+}}$ in the order: B-15-C-5 (**20b**) 18-C-6 (**20c**) > DB-18-C-6 (**15**) >> DB-24-C-8 (**17**).¹¹⁵

Neutral inorganic complexes of uranium and plutonium were shown^{134, 135} to be linked to the macrocycle by means of hydrogen bonds through coordinated water molecules. These characteristic features of the structures of uranium and plutonium complexes could explain why the principle of geometric correspondence does not operate in this case.

b. Methods for increasing extraction efficiency and non-conventional extraction systems

The major routes to increasing the distribution coefficients in the extraction systems based on crown ethers are as follows: introduction of an additional extractant in order to achieve an extraction

synergism effect, addition of a complexation agent (EDTA, acetylacetone, *etc.*) to the aqueous phase, addition of a polar water-miscible solvent (acetonitrile, propylene carbonate, dioxane, *etc.*) to the aqueous phase, extraction by crown ethers dissolved in liquid CO₂, the use of biphasic aqueous systems for extraction.

The synergism of extraction is understood as a joint action of two extractants, which results in the distribution coefficients exceeding those for each extractant used separately. Systems involving crown ethers were developed and the synergetic effects in the extraction of ions of cobalt,¹³⁶ manganese,^{137–139} palladium,¹⁴⁰ uranium(VI),¹⁴¹ lanthanides and actinides,^{142–149} strontium and barium,^{150–153} cesium²⁵ and radium^{154, 155} were studied. Unfortunately, in the studies of synergism the major attention has been paid to quantitative parameters of the extraction process (calculation of extraction constants and distribution coefficients), while the reasons for this effect and its mechanism have rarely been discussed. An exception are the studies by McDowell *et al.*¹²⁸ and Meguro *et al.*¹⁴⁸ who investigated the influence of the macrocycle structure on extraction synergism. In the extraction of lanthanides and actinides, which have high coordination numbers, the reason for the synergism seems to consist in the replacement of water molecules of coordination by the first extractant, which facilitates the transfer of the adduct with the second extractant to the organic phase.

In a number of cases, it was possible to increase substantially the distribution coefficients by adding a polar water-miscible organic solvent to the extraction system. It was shown^{106, 107, 156} that organic solvents less polar than water (acetonitrile, propylene carbonate) favour formation of neutral complexes, *e.g.*, of UO₂(NO₃)₂ or Pu(NO₃)₄, with crown ethers, which enhances strongly the extraction efficiency.

Rather recently,¹⁵⁷ liquid CO₂ has been proposed as a solvent for crown ether-assisted extraction. The main advantage of this method consists in a substantial decrease in the amount of liquid waste containing as a rule toxic organic solvents. Furthermore, the high diffusive ability and low viscosity of liquid CO₂ allows direct extraction of dissolved substances from the solid phase (*e.g.*, from samples of ground, soil, sand, *etc.*). In his review, Wai considered the effect of solubility of ligands and metal complexes in CO₂, pH of the aqueous phase, temperature and pressure, the chemical nature of metal compounds and other factors on the extraction efficiency.¹⁵⁷ An interesting feature of this extraction technique consists in the possibility of separation of metal compounds in organic and inorganic forms by selecting appropriate ligands.

Biphasic aqueous extraction systems represent mixtures of water-soluble polymers, inorganic salts and extractants which separate and form immiscible phases.^{158–160} The advantages of these systems reside in the use of inexpensive, non-toxic and easily accessible water-soluble polymers and in the possibility of using novel water-soluble complexants, which is particularly attractive in the case of dicyclohexano- and non-substituted crown ethers. The application of water-soluble 15-C-5 (**20b**) and 18-C-6 (**20c**) as extractants for cations of metals of groups I and II, UO₂²⁺, Pu⁴⁺, Th⁴⁺ and Am³⁺ in a biphasic aqueous system containing poly(ethylene glycol) (PEG-2000) and (NH₄)₂SO₄ has been described.^{135, 160} The distribution coefficient of UO₂²⁺ ($D_{UO_2^{2+}}$) exceeded unity at a rather high concentration of 18-C-6 (**20c**) (1.25 mol litre⁻¹).¹³⁵

2. The use of crown ethers in radiochemical analysis

a. Determination of the content of radionuclides in water, soil and biological materials

Isotopes of uranium and plutonium as well as their fission products, *viz.*, the radionuclides ⁹⁰Sr and ¹³⁷Cs, are extremely toxic. In this connection, the determination of concentrations of these radionuclides in various natural specimens, which can find their way into human and animal organisms, is of great importance. This analysis is difficult to perform due to the presence of a great amount of interfering cations (Na⁺, K⁺, Mg²⁺, Ca²⁺, *etc.*).

From the biological viewpoint, the isotope ^{90}Sr is one of the most hazardous fission products, since it can replace calcium in bones and has a long half-life time. Numerous procedures have been developed to date for the determination of the content of ^{90}Sr in water, soil and biological samples. These include precipitation,¹⁶¹ liquid extraction,¹⁶² ion exchange,^{163–165} thin-layer chromatography¹⁶⁶ and other methods. All these techniques have serious disadvantages, which prevents their wide uses. Thus in the case of inadvertent release of radionuclides resulting from accidents at an atomic energy power plant or from those related to tests and production on nuclear weapons, a fast, simple and efficient method is required. However, most of the above-mentioned methods of analysis are lengthy.¹⁶⁷ The use of macrocyclic compounds allows considerable simplification of the analytical procedure.

Using the sorbent Sr-Spec, Horwitz *et al.*^{21,22} succeeded in developing a number of competitive methods for the determination of strontium against the background of a large amount of cations which are not biologically hazardous. Gjerci¹⁶⁸ proposed an extraction-chromatographic method for the determination of the content of radioactive strontium in soil, grasses, milk and animal bones. A sample under analysis is subjected to extraction, filtered and then strontium is precipitated from the filtrate as oxalate, the precipitate is dissolved in 3M HNO_3 and the resulting solution is passed through a column with Sr-Spec. The strontium sorbed selectively is eluted and quantitated. Vajda *et al.*¹⁶⁹ reported a method which allows determination of up to 80% of radioactive strontium in soil. This method consists in the separation of potassium, sorption of strontium on Sr-Spec and subsequent precipitation of strontium as oxalate. The Sr-Spec sorbent was also used¹⁷⁰ for rapid quantitation of ^{90}Sr in radioactive waste solutions in nitric acid in the presence of radionuclides of Am, Cd, Co, Ce, Sn, Cs and Y with separation factors $> 99\%$. A continuous automated method for the analysis of ^{90}Sr (see Ref. 171) and a procedure for the determination of ^{90}Sr in water and sedimentary rocks based on the sorbent Sr-Spec were proposed.¹⁷² In this case, ^{90}Y (^{90}Sr) is determined by liquid scintillation after separation of strontium on a column packed with Sr-Spec.¹⁷²

The Sr-sorption abilities of two DCH-18-C-6 (**12**)-based solvents prepared by different techniques were compared and a new method for the quantitation of strontium in natural waters was proposed.¹⁷³ One of them, *viz.*, SESys, was obtained by introducing a crown ether into a matrix of a styrene–divinylbenzene copolymer during polymer isolation, while the other sorbent (impregnate) was prepared by impregnating a macroporous styrene–divinylbenzene copolymer with the same crown ether. Higher values of the distribution coefficient D_{Sr} were obtained on this porous polymeric sorbent.

Extraction-chromatographic and extraction methods were proposed^{45, 174, 175} for rapid quantitation of radioactive strontium in water, soil and agricultural products. An impregnate containing a 10% solution of DCH-18-C-6 (**12**) was used as the sorbent,⁴⁵ while the extraction system was composed of 10% solution of the crown ether **12** in chloroform.^{174, 175} The analytical procedure involved drying of the sample, its calcination at 500–600 °C for several hours and subsequent treatment of the ash with HNO_3 or HCl . Then the solution obtained was passed through a sorption column for binding strontium or recourse was made to extraction, strontium was isolated and its β -activity was measured. In this method, analysis of a sample after its pretreatment required no more than 30–50 min, the chemical yield was $> 95\%$ with the product purity $> 98\%$.⁴⁵

A rapid method for the quantitation of Sr in milk was developed.¹⁷⁶ Milk was treated with a chelate-forming resin, Sr was eluted with a dilute nitric acid, separated from Ca by extraction of the eluate with DCH-18-C-6 (**12**) in chloroform with subsequent transfer of Sr to the aqueous solution and removal of Ba by extraction with a solution of 21-C-7 in dichloromethane. This analytical procedure takes about 3 h and more than 90% of strontium is determined.

Separation and concentration of a number of radionuclides based on co-precipitation of metal ions with silicotungstic acid ($\text{H}_4\text{SiW}_{12}\text{O}_{40} \cdot 2\text{H}_2\text{O}$) from 1M HNO_3 in the presence of 15-C-5 (**20b**) and 18-C-6 (**20c**) were carried out.^{177–180} The selectivity of separation of radionuclides depends on the ratio of the stability constants of crown-ether complexes with the metal cations present in the solution. Precipitation was used to separate and concentrate Sr in the presence of Ca;¹⁷⁹ Pb in the presence of Ca, Sr and Ba,¹⁷⁸ Ra in the presence of Ca and Sr.¹⁷⁷ This method allows estimation of the stability constant of a radionuclide complex with a crown ether even at a very low radionuclide content in solution.¹⁷⁷

A method was devised¹⁸¹ for the determination of the content of alkali and alkaline-earth metals in natural water using ion-exchange chromatography with a conductometric detector. Non-modified silica gel was used as the ion-exchange material, and the eluent contained oxalic acid ($0.001 \text{ mol litre}^{-1}$) and 18-C-6 (**20c**) ($0.003 \text{ mol litre}^{-1}$).

Miura *et al.*¹⁸² proposed a method for the determination of ^{210}Pb and ^{210}Po in sedimentary rocks, clay and biological specimens. The analytical procedure includes four stages: sample decomposition, co-precipitation of ^{210}Pb and ^{210}Po with CuS , separation of isotopes on a column with Sr-Spec and quantitation of ^{210}Pb and ^{210}Po .

Calix[4]arene-crown-6 and calix[4]arene-crown-5 containing two allyl groups were synthesised and grafted onto silica gel.⁹² The macrocycle/silica gel ratio was 1 : 10 (w/w). These sorbents were successfully used for the chromatographic separation of Cs^+ from cations of other alkali metals.

Mohite *et al.*¹⁸³ proposed a chromatographic method for the determination of barium in minerals. A copolymer of DB-18-C-6 (**15**) with formaldehyde was used as the sorbent. The absorbed barium was eluted with 1M acetic acid and its content was determined spectrophotometrically with Sulfonazo III. The capacity for barium was equal to $1.475 \text{ mmol g}^{-1}$. This method allows separation of barium from lead, thorium, uranium, cesium, cerium and molybdenum. The procedure is reproducible with an error of $\pm 2\%$.

The last-mentioned authors^{126, 127} have also described the application of extraction and column chromatography for the quantitation of uranium in geological specimens and animal bones. Dibenzocrown ethers were used as the extractants, while the sorbent was a copolymer of DB-18-C-6 (**15**) with formaldehyde with a sorption capacity of 2.5 mmol g^{-1} . Both methods are distinguished by their simplicity, rapidity and good reproducibility and allow separation of uranium from nuclear fission products.

b. Separation of isotopes

In recent years, considerable progress has been observed in the separation of metal isotopes using extraction and sorption systems based on crown ethers. A monograph by Hiraoka¹⁸⁴ published about 15 years ago cited only one report describing a method of separation of calcium isotopes with the aid of crown ethers. A review by Tsivadze *et al.*¹⁸⁵ published in 1996 generalises the results of over 40 similar studies and presents examples of the use of crown-containing systems for the separation of isotopes of hydrogen, lithium, sodium, potassium, strontium, barium, zinc, cerium and uranium. Kim *et al.*¹⁸⁶ reported recently the application of a polymeric resin based on an azacrown ether for the separation of lithium isotopes. Methods are known for the extraction-based separation of potassium isotopes with the aid of DCH-18-C-6 (**12**)¹⁸⁷ and chromatographic enrichment of calcium isotopes using 18-C-6 (**20c**) grafted onto a macroporous solid support.^{188, 189} An anomalous isotope effect for the isotopes with even and odd mass numbers was observed in the extraction of isotopes of zinc,^{190, 191} magnesium,¹⁹² samarium¹⁹³ and strontium¹⁹⁴ with crown ethers.

The development of methods for the isolation of a daughter isotope ^{90}Y from the parent isotope ^{90}Sr is an important and interesting direction. The isotope ^{90}Y has found wide uses in biology and radiotherapy owing to its short half-life time (64 h)

and stability of its daughter isotope ^{90}Zr . From the viewpoint of clinical application of ^{90}Y , its purification from ^{90}Sr is particularly important. It was found that this problem may successfully be solved using certain crown ethers. Thus ^{90}Y with the purity $> 99.9\%$ was obtained by liquid extraction based on benzocrown ethers having a carboxy substituent in their polyether ring.¹⁹⁵ Chuang and Lo¹⁹⁶ studied the extraction of strontium and yttrium cations by solutions of DCH-18-C-6 (**12**), 18-C-6 (**20c**), B-15-C-5 (**21b**) and DB-18-C-6 (**15**) in chloroform and showed that DCH-18-C-6 (**12**) is the most efficient in the separation of these isotopes. This method of separation is remarkable for its simplicity. The separation proceeds with quantitative yields and the purity achieved is above 99.9%. The isotopes ^{90}Y and ^{90}Sr were separated chromatographically on a paper impregnated with carboxy-substituted benzocrown ethers¹⁹⁷ and on a column packed with a dibenzocrown ether–formaldehyde copolymer.¹⁹⁸ A method of extraction-chromatographic separation of ^{90}Y from ^{90}Sr by sorption with DCH-18-C-6 (**12**) immobilised on silica was proposed.⁴² Quantitation of strontium and separation of its daughter isotope Y^{3+} by thin-layer chromatography on SiO_2 with DCH-18-C-6 (**12**) applied on it was described.¹⁹⁹

V. Conclusion

Crown ethers possess high selectivity and complexation efficiency, resistance to irradiation and a number of other advantages. The progress in the chemistry of macrocyclic polyethers made it possible to develop methods of quantitation of highly toxic radionuclides in various mineral and biological specimens, as well as a number of promising processes for the reprocessing of spent nuclear fuel and utilisation of radioactive waste. A new direction of the use of crown ethers in radiochemistry is the extraction with the aid of liquid CO_2 .

Upon irradiation of both free crown ethers and extraction systems based on them, the main process of radiolysis is the macrocycle scission; however, the radiation-chemical yield of the ring opening is insignificant at absorbed doses corresponding to real conditions.

However, the studies of radiation chemistry of crown ethers and the development of methods for their immobilisation on supports face some unsolved problems. Thus details of the mechanism of radiolysis of crown ethers remain virtually obscure, there is no information about the structure and transformations of primary products. The radiation chemistry of calixarene-crown ethers is virtually uninvestigated.

Definite advances have been achieved in the synthesis of impregnates based on dicyclohexanocrown ethers. A number of procedures for the determination of strontium, lead, polonium and other elements have been developed based on the sorbent Sr-Spec. Unfortunately, the high solubility of non-substituted crown ethers in water apparently will not allow creation of impregnates based on them, unless the polyether ring of crown ethers is modified by hydrophobic groups. The methods of chemical immobilisation of dicyclohexano- and non-substituted crown ethers developed to date are mostly based on the condensation of the macrocycles containing reactive groups. These methods are complicated, include many steps and are time-consuming; therefore, their perfection is needed. In this context, of high interest might be the use of methods of radiation-chemical synthesis, which would allow selective single-step formation of active centres and their addition to the reactive groups of a support or a monomer.

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^a — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*

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^h — *Radiochemistry (Engl. Transl.)*

ⁱ — *Mendelev Chem. J. (Engl. Transl.)*

Arene complexes of rare-earth metals

M N Bochkarev

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Abstract. Data on syntheses, structures and reactivities of scandium, yttrium, lanthanum and lanthanide complexes with π -bonded ligands containing one or several six-membered aromatic rings are surveyed and systematised. The bibliography includes 107 references.

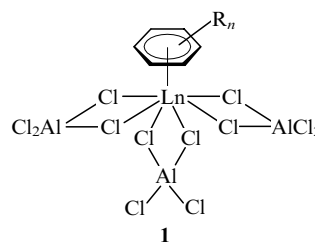
I. Introduction

Early investigations in the field of chemistry of organometallic compounds containing rare-earth metals were aimed at synthesising and studying compounds typical of organometallic chemistry, such as σ -alkyl(aryl), cyclopentadienyl, indenyl, fluorenyl, cyclooctadienyl, *etc.* derivatives. Complexes containing π -bonded arene ligands were studied later.¹ However, the chemistry of these compounds was extensively investigated in the last 12 years after the first benzene derivatives of lanthanides had been synthesized. The accumulated data allow some general conclusions to be drawn about the characteristic features of the synthesis, structures, the character of metal–ligand bonding and reactivity of π -arene lanthanide complexes belonging to a class of compounds unique in many respects. Particular types of π -arene lanthanide complexes were surveyed in the reviews.^{2,3} The present review is devoted to comprehensive and critical consideration of the available data on the synthesis, structures, the character of bonding, reactivity and catalytic activity of rare-earth metal complexes containing π -bonded six-membered aromatic rings, which were published before January 2000. Derivatives of stilbene, tolan and analogous compounds fall outside the scope of this review because π -electrons of multiple bonds of substituents in aromatic rings of these compounds are generally involved in Ln ligand interactions.

II. Complexes of rare-earth metals with derivatives of benzene and its homologues

1. Arene chloroaluminate complexes

The chloroaluminate complex of samarium, $(C_6Me_6)Sm(AlCl_4)_3$, was the first complex of a rare-earth metal with a π -bonded arene ligand synthesised under conditions of the Friedel–Crafts reaction.^{4–6} This procedure for the synthesis was extended to other complexes of the type **1**. The reactions were carried out with 1,3- $Me_2C_6H_4$,⁷ C_6H_6 ,^{8–10} $Me_4C_6H_2$,^{11,12} MeC_6H_5 (see Ref. 13) and a large series of lanthanides (Y, Pr, Nd, Gd,¹² La,⁸ Eu and Yb¹³). The compositions and structures of complexes of the type **1** indicate that the aromatic moiety is η^6 -coordinated to the trivalent metal atom and serves as a neutral π -donor ligand. The average Ln–C distances [2.93 Å (Nd),¹¹ 2.90 Å (Sm),⁷ 2.999 Å (Eu)¹⁴ and 2.978 Å (Yb)¹⁵] are noticeably shorter than the sums of the van der Waals radius of the carbon atom and the ionic radius of the corresponding metal atom, but are substantially longer than the Ln–C contacts in the cyclopentadienyl derivatives (2.60–2.82 Å for the whole series of lanthanides).



Ln = Y, Pr, Nd, Gd, La, Eu, Yb; R = H, Me; $n = 0, 1, 2, 4$.

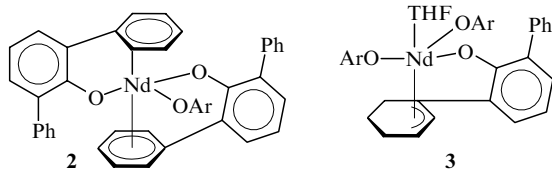
The replacement of one of the bridging chlorine atoms by the alkyl group, for example, in the complexes $(C_6H_5Me)Ln.(AlCl_3Me)_3$ (Ln = Y or Nd) and $(C_6H_5Me)Nd(AlBr_3Et)_3$,¹² does not lead to a change in the character of the arene–metal bond. The divalent europium complex $(C_6Me_6)Eu(AlCl_4)_2$ has an analogous structure.¹⁴

2. Arene aryloxy complexes

In aryloxides of lanthanides, there are nonvalent interactions between the metal atom and the benzene ring identical to those found in arene chloroaluminate complexes. The presence of the phenyl substituent at the *ortho* position of the aryloxy group [for

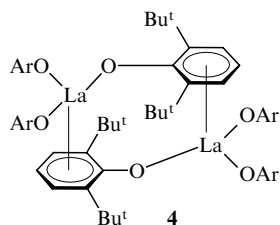
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example, in the complex $\text{Nd}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3$ (**2**) results in an intramolecular η^6 -interaction between the lanthanide atom and one of the phenyl substituents of the phenoxy ligand. The phenyl substituent in the second phenoxy ligand is η^1 -bonded to the Ln atom, whereas the third phenoxy ligand remains monodentate.^{15–17} In the analogous complex $\text{Nd}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3(\text{THF})$ (**3**), which differs by the presence of one THF molecule coordinated to the metal atom, only one $\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6}$ substituent serves as a chelate ligand, the multiplicity of the Ln–Ph π -bond decreasing (becoming triple).¹⁶



Ar = 2,6- $\text{Ph}_2\text{C}_6\text{H}_3$.

In lanthanide triphenoxides containing the *tert*-butyl substituents at positions 2 and 6, the metal atom is η^6 -bonded to the phenoxide ligand to form the dimers $(2,6\text{-Bu}_2\text{C}_6\text{H}_3\text{O})_2\text{Ln}(\mu\text{-}2,6\text{-Bu}_2\text{C}_6\text{H}_3\text{O})_2\text{Ln}(\text{OC}_6\text{H}_3\text{Bu}_2\text{-2,6})_2$ (**4**).^{18, 19}



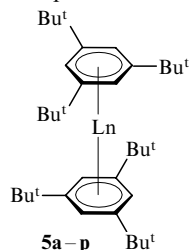
Ar = 2,6- $\text{Bu}_2\text{C}_6\text{H}_3$.

The Ln–Arn contacts (Arn is arene) are retained upon dissolution of complexes of the type **4** in nonsolvating solvents. However, π -bonds are cleaved in THF or upon addition of ammonia and the coordination site of the η^6 -arene ligand in the resulting complexes is occupied by solvent molecules, which is indicative of low strength of the Ln–Arn bond. The Ln–C bond lengths in these fragments (the average distances are 2.986–3.061 Å) are virtually identical to the corresponding values in arene chloroaluminate complexes.

3. Bisarene complexes

Co-condensation of benzene and neodymium vapours on a surface cooled to -196°C afforded a binuclear complex with composition $\text{Nd}_2(\text{C}_6\text{H}_6)_3$,²⁰ which was isolated as black insoluble crystals. The magnetic moment ($3.42 \mu_B$) corresponds to the Nd(III) cation ($3.68 \mu_B$ ²¹) and the dianionic form of all three benzene ligands. The complex was not studied by X-ray diffraction analysis, but it is reasonable to suppose that its structure is similar to that of the thulium naphthalene analogue $[(\text{C}_{10}\text{H}_8)\text{Tm}(\text{DME})]_2(\mu\text{-C}_{10}\text{H}_8)$ considered below.

Sandwich bisarene complexes of rare-earth metals of the $(1,3,5\text{-Bu}_3\text{C}_6\text{H}_3)_2\text{Ln}$ type (**5**) analogous to the well-known bisarene complexes of *d* transition metals were prepared by coconden-

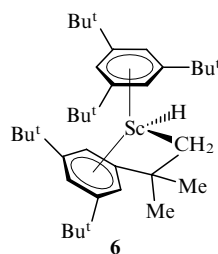


Ln = Gd (**a**), Y (**b**), Ho (**c**), Nd (**d**), Tb (**e**), Dy (**f**), Er (**g**), Lu (**h**), Ce (**i**), Eu (**j**), Yb (**l**), La (**m**), Pr (**n**), Sm (**o**), Sc (**p**).

sation of 1,3,5-tri-*tert*-butylbenzene and metal vapours at 75 K.^{22–25} The structures and magnetic moments of the complexes **5** confirm the η^6 -character of the bond between the neutral aromatic ring and the formally zero-valent metal atom.

In gadolinium complex **5a** characterised by X-ray diffraction analysis, the Gd–C distances are in the range of 2.585–2.660 Å (the average distance is 2.630 Å). These distances are virtually identical to the Ln–C bond lengths in cyclopentadienyl complexes of the Cp_2GdBr type (2.635, 2.639 and 2.630 Å²⁶). The yttrium (**5b**) and holmium (**5c**) complexes were found to have analogous structures.^{3, 22}

The stability of the compounds **5** depends on the nature of lanthanide. Thus the Yb, Nd, Gd, Tb, Dy, Ho, Er and Lu complexes are stable (some of them can be sublimed *in vacuo* without decomposition), whereas the Ce, Eu, Tm and Yb complexes do not form stable products. Derivatives of La, Pr and Sm are intermediate in stability. In the synthesis of the scandium complex, the formation of the expected sandwich $(1,3,5\text{-Bu}_3\text{C}_6\text{H}_3)_2\text{Sc}$ (**5p**) was accompanied by the formation of the complex $(\eta^6\text{-Bu}_3\text{C}_6\text{H}_3)[\eta^6, \eta^1\text{-Bu}_2(\text{CMe}_2\text{CH}_2)\text{C}_6\text{H}_3]\text{ScH}$ (**6**) containing Sc(II) due to the insertion of Sc at the C–H bond of the methyl group of the substituent.²⁷

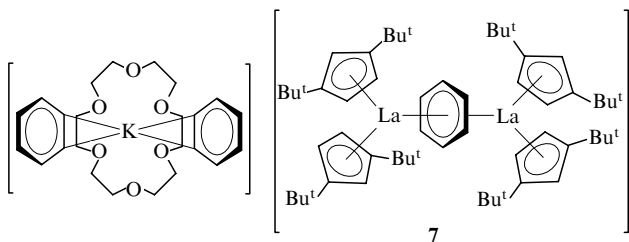


Since a strong arene–lanthanide π -bond can be formed if the metal atom adopts the d^1s^2 configuration, the difference in thermal stability of the complexes **5** was attributed to the difference in energy of promotion of $f^n s^2 \rightarrow f^{n-1} d^1 s^2$ transitions for different lanthanides. Thermodynamic studies²⁵ confirmed the high stability of Ln–Arn bonds in bisarene complexes. Thus the enthalpies of cleavage of these bonds in the Yb, Gd, Dy, Ho and Er complexes are 72, 68, 47, 56 and 57 kcal mol^{–1}, respectively.²⁵

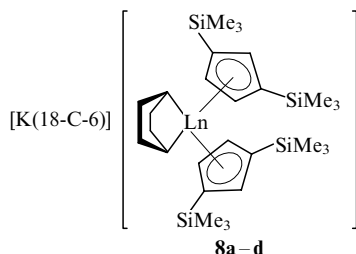
The stability of bisarene complexes increases as the number and size of substituents in the aromatic ring increase as was exemplified by scandium derivatives.³ Calculations by molecular mechanics²⁸ for $(\text{C}_6\text{H}_6)_2\text{Gd}$ and $(1,3,5\text{-Bu}_3\text{C}_6\text{H}_3)_2\text{Ln}$ (**5**) [Ln = Gd (**a**), Y (**b**) or Yb (**l**)] confirmed that the benzene complex is substantially less stable than the complexes **5a, b, l** containing the *tert*-butyl groups in the benzene ring. Quantum-chemical calculations^{29, 30} demonstrated that the metal atoms are bound to the benzene ligands primarily through back donation from the occupied $d_{\pm 2}$ orbitals of the metal atom to the unoccupied π -orbitals of the benzene ligands.

4. Complexes with benzene radical anions and dianions

Reduction of the cyclopentadienyl complex of lanthanum containing two *tert*-butyl substituents in the cyclopentadienyl rings, *viz.*, $\text{Cp}_2^{\text{t}}\text{La}$, where $\text{Cp}^{\text{t}} = \eta^5\text{-C}_5\text{H}_3\text{Bu}_2\text{-1,3}$, with an excess of potassium in benzene in the presence of 18-crown-6 (18-C-6) afforded a dark-red product. Subsequent heating of the latter in benzene at 70°C gave rise to the dark-green ate-complex $[\text{K}(18\text{-C-6})(\eta^2\text{-C}_6\text{H}_6)_2][(\text{Cp}_2^{\text{t}}\text{La})(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_6)]$ (**7**).³¹ X-Ray diffraction analysis demonstrated that the bridging six-membered ring in the anionic moiety of the complex **7** is planar and the C–C bond lengths in this ring are almost identical. All La–C(benzene) bond lengths vary over a narrow range (2.75–2.79 Å). Based on these data, the structure of a salt containing two $\text{Cp}_2^{\text{t}}\text{La}(\text{II})$ units η^6 -bonded to the benzene anion was assigned to the complex **7**.



An analogous reaction of potassium with the complexes $\text{Cp}^{\text{ts}}\text{Ln}$ [$\text{Cp}^{\text{ts}} = \text{C}_5\text{H}_3(\text{SiMe}_3)_2$ -1,3; $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$ or Nd] also afforded dark-red ionic complexes $[\text{K}(18\text{-C-6})][\text{Cp}^{\text{ts}}\text{Ln}(\text{C}_6\text{H}_6)]$ (**8a–d**). However, the cations in these complexes do not contain coordinated benzene molecules and the C_6H_6 ligand in the anionic moiety exists as the dianion of cyclohexa-1,4-diene η^6 -bonded to the $\text{Cp}^{\text{ts}}\text{Ln}$ unit with the trivalent Ln atom.^{32,33} In the complex **8a**, two short $\text{La} - \text{C}(\text{cyclohexadiene})$ distances are 2.617 and 2.652 Å. In analogous complexes of cerium and neodymium **8b,c**, the corresponding bond lengths are 2.588 and 2.612 Å (Ce) and 2.555 and 2.572 Å (Nd).

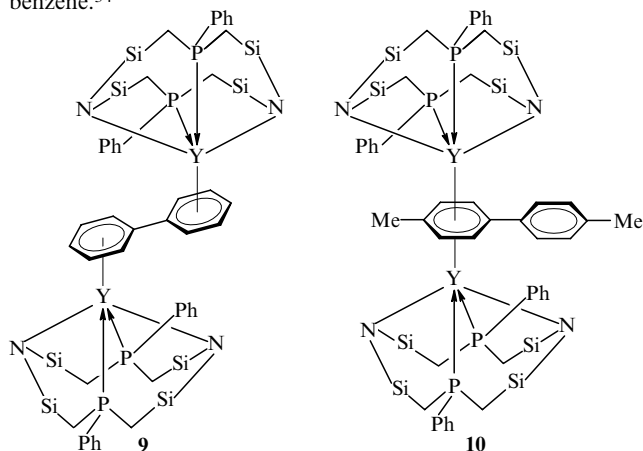


$\text{Ln} = \text{La}$ (a), Ce (b), Nd (c), Pr (d).

ESR studies demonstrated³³ that reduction of $\text{Cp}^{\text{ts}}\text{La}$ with potassium in benzene in the presence of 18-C-6 afforded at least four metal-centred free-radical species. The authors believed that the latter are $\text{La}(\text{II})$ derivatives. In this stage, the reaction mixture was dark-blue-violet in colour, which then changed to dark-red.

5. Biphenyl complexes

Treatment of the yttrium(III) chloride complex with composition LYCl , where $\text{L} = \text{PhP}[\text{CH}_2(\text{SiMe}_2\text{N}(\text{SiMe}_2)\text{CH}_2)_2\text{PPh}]$, with phenyllithium gave rise to the dark-blue binuclear product $(\{\text{PhP}[\text{CH}_2(\text{SiMe}_2\text{N}(\text{SiMe}_2)\text{CH}_2)_2\text{PPh}\}\text{Y})_2(\mu\text{-PhPh})$ (**9**)[†] containing the biphenyl dianion as the bridging ligand.³⁴ The complex **9** was also prepared by the reaction of the σ -alkyl complex $\text{LYCH}_2\text{SiMe}_3$ [$\text{L} = \text{PhP}[\text{CH}_2(\text{SiMe}_2\text{N}(\text{SiMe}_2)\text{CH}_2)_2\text{PPh}]$] with benzene.³⁴



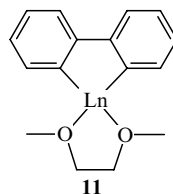
In the complex **9**, both rings in the biphenyl ligand remain virtually planar and the $\text{Y} - \text{C}$ distances vary over a narrow range (2.675–2.738 Å), which are evidence of η^6 -interaction. These

[†] Hereinafter, the methyl groups at the silicon atoms are omitted.

distances (the average distance is 2.723 Å) are close to the $\text{Y} - \text{C}$ bond lengths in the complex $\text{Cp}_3\text{Y}(\text{THF})$ (the average distance is 2.71 Å)³⁵ and are somewhat larger than those in the complexes $[\text{Cp}_2\text{YCl}]_2$ (2.60 Å)³⁶ and $(\text{C}_5\text{Me}_5)_2\text{YCl}(\text{THF})$ (2.659 Å).³⁷

The reaction of LYCl with $3\text{-MeC}_6\text{H}_4\text{Li}$ also resulted in the formation of a $\text{C} - \text{C}$ bond. According to the data of ^1H NMR and UV spectroscopy, the dark-blue reaction product is structurally similar to the complex **9**. However, $4\text{-MeC}_6\text{H}_4\text{Li}$ under the same conditions gave the dark-brown compound $(\{\text{PhP}[\text{CH}_2(\text{SiMe}_2)\text{N}(\text{SiMe}_2)\text{CH}_2)_2\text{PPh}\}\text{Y})_2(\mu\text{-MePhPhMe})$ (**10**) in which both YL fragments are bound to the same ring of the $[\text{MeC}_6\text{H}_4\text{C}_6\text{H}_4\text{Me}]^{2-}$ anion.³⁴ The average $\text{Y} - \text{C}$ distances in the fragments of **10** (2.676 and 2.699 Å) are somewhat shorter than the corresponding bond lengths in the complex **9**. ^1H NMR spectral studies of the complex **10** demonstrated that slow (within the NMR time scale) migration of one of the YL groups from one benzene ring to another occurs in solution. It was assumed³⁴ that such behaviour in solutions is also typical of other complexes with bridging $\text{Ar} - \text{Ar}$ ligands.

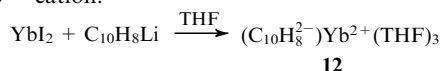
Samarium and ytterbium powders activated with diiodoethane reacted with biphenylene at room temperature to form dark-coloured solutions.³⁸ Attempts to isolate reaction products in the individual state failed. However, their reactions with oxygen (giving rise to 1,1'-biphenyl-2,2'-diol), deuteromethanol (yielding a mixture of biphenyl and dideuterobiphenyl) and Me_2SiCl_2 (forming a mixture of biphenyl and 1,1-dimethylsilafluorene) were carried out. These results testify that the reactions of lanthanides with biphenylene lead to the cleavage of the four-membered ring giving rise to the lanthanide σ -complexes with biphenyl (**11**). It was suggested³⁸ that the first stage involved reduction of biphenylene to form the ionic intermediates $\text{C}_{12}\text{H}_8^{2-}\text{Ln}^{2+}$, which abstracted hydrogen from the solvent to form biphenyl and the complex **11**.



Apparently, an analogous product was formed in the reaction of octamethylbiphenylenedilithium with SmI_2 .³⁸

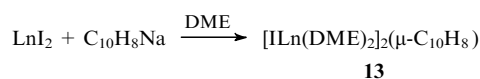
III. Complexes with naphthalene derivatives

It was found that reduction of anhydrous ytterbium diiodide with two equivalents of lithium naphthalenide in THF or dimethoxyethane (DME) afforded insoluble black pyrophoric powders with composition $(\text{C}_{10}\text{H}_8)\text{Yb}(\text{THF})_3$ or $(\text{C}_{10}\text{H}_8)\text{Yb}(\text{DME})$.^{39–44} Based on the facts that the resulting compounds are diamagnetic [$\text{Yb}(0)$ is diamagnetic] and their reactivities are surprisingly high (even for organolanthanides), it was originally conceived that these products are complexes of zero-valent ytterbium π -bonded to the neutral naphthalene ring. However, additional data on tetrahydrofuran complex **12** obtained more recently demonstrated that these compounds in fact contain the naphthalene dianion and the Yb^{2+} cation.



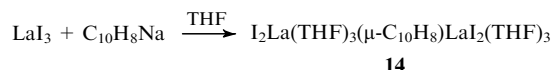
Analogous naphthalene complexes with samarium and europium^{43,45–48} as well as 1-methylnaphthalene complex with ytterbium^{40,48} were synthesised. The naphthalene complexes of samarium, europium and ytterbium, like alkali metal naphthalenides, are powerful reducing agents. However, the former complexes in contrast to naphthalenides do not react with naphthalene [the reactions could form radical-anionic derivatives of the type $(\text{C}_{10}\text{H}_8^-)_2\text{Ln}(\text{THF})_x$].

The reactions of equimolar amounts of LnI_2 ($\text{Ln} = \text{Eu}$ or Yb) and sodium naphthalenide resulted in the replacement of only one iodide anion and afforded binuclear derivatives **13** containing the bridging naphthalene dianion rather than radical-anionic complexes $(\text{C}_{10}\text{H}_8^{\cdot-})\text{LnI}(\text{THF})_x$.^{49,50}

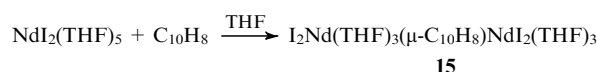


$\text{Ln} = \text{Eu}, \text{Yb}$.

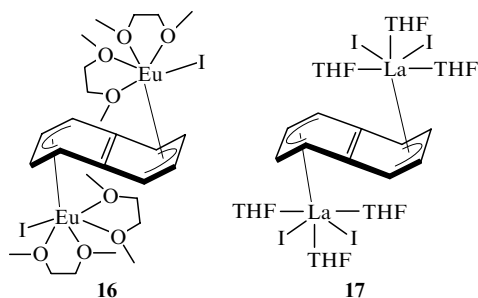
The $\text{Ln}(\mu\text{-C}_{10}\text{H}_8)\text{Ln}$ moiety containing the naphthalene bridging dianion (complex **14**) was also formed in the reaction of sodium naphthalenide with lanthanum iodide.⁴⁹ Analogous complexes were obtained for Ce, Pr, Nd and Gd.⁵⁰



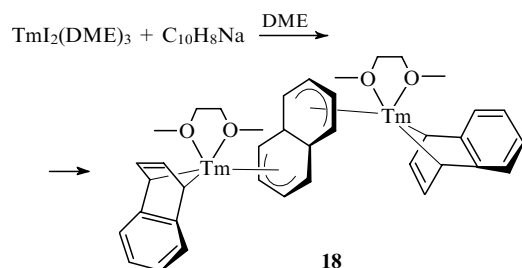
The stability of complexes of the type **14** decreases on going from light to heavy lanthanides. From Tb and onwards, attempts to isolate such complexes failed even at low temperature. The neodymium derivative **15** was synthesised by oxidation of divalent neodymium iodide with naphthalene in a solution in THF.⁵¹



The naphthalene complexes of europium and lanthanum, *viz.*, $[\text{I}_2\text{Eu}(\text{DME})_2]_2(\mu\text{-C}_{10}\text{H}_8)$ (**16**) and $[\text{I}_2\text{La}(\text{THF})_3]_2(\mu\text{-C}_{10}\text{H}_8)$ (**17**), respectively, were studied by X-ray diffraction analysis.⁴⁹ In these complexes, the metal atoms are located on the opposite sides of the plane of the bridging naphthalene ligand and are η^4 -bonded to different rings. The naphthalene moiety is nonplanar and the dihedral angles between the rings are 5.8° and 15.2° in the complexes **16** and **17**, respectively. The shortest La–C and Eu–C distances are in the ranges of 2.782–2.808 and 2.815–2.858 Å, respectively.



With the aim of preparing halogen-free naphthalene complexes of lanthanides, the reactions of triiodides LnI_3 with a threefold excess of $\text{C}_{10}\text{H}_8\text{Na}$ were carried out.^{43,52} After removal of the solvent, solid black or dark-brown amorphous substances were obtained from the resulting dark-brown solutions. Attempts to isolate individual products from these substances failed. The individual compound $[\text{C}_{10}\text{H}_8\text{Tm}(\text{DME})]_2(\mu\text{-C}_{10}\text{H}_8)$ (**18**) was obtained only for thulium starting from the salt $\text{TmI}_2(\text{DME})_3$.⁵³



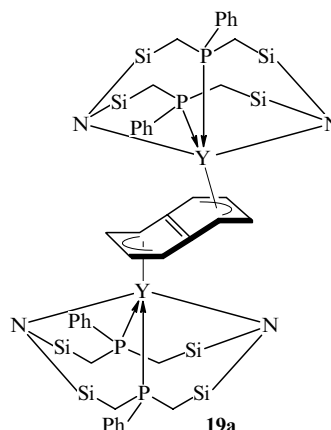
It is worthy of note that thulium was oxidised in the course of the reaction to the trivalent state in spite of the fact that $\text{C}_{10}\text{H}_8\text{Na}$

is a strong reducing agent. The trivalent state of thulium was confirmed by magnetic measurements and by the fact that the colour of the reaction mixture changed from green to red-brown. The compound **18** has the structure of a triple-decker sandwich. According to the valence balance, all three naphthalene groups in the complex exist as dianions. The central binuclear unit with the η^4 : η^4 -bonded bridging naphthalene ligand is structurally similar to those in the iodine-containing complexes **16** and **17**.

The lengths of the short $\text{Tm}-\text{C}(\text{bridging } \text{C}_{10}\text{H}_8)$ bonds are in the range of 2.59–2.62 Å. The folding angle of the rings along the $\text{C}(1)-\text{C}(4)$ line is 19.28° . Based on the shortest $\text{Tm}-\text{C}$ distances to the terminal naphthalene moieties [2.41 and 2.42 Å for $\text{C}(\alpha)$ and 2.54 and 2.54 Å for $\text{C}(\beta)$], both types of interactions can be considered as η^4 and η^2 . However, the dihedral angle (26.22°) and the redistribution of the C–C bond lengths in the coordinated rings correspond to cyclohexa-1,4-diene. The absolute values of the shortest $\text{Tm}-\text{C}$ distances are identical (taking account of the difference in the ionic radii and coordination numbers of the metal atoms) to the $\text{Ln}-\text{C}$ σ -bonds in the complexes $[\text{Li}(\text{THF})_3] \cdot \{[(\text{Me}_3\text{Si})_2\text{CH}]_3\text{YbCl}\}$ (the average distance is 2.375 Å),⁵⁴ $\text{Cp}^*\text{CeCH}(\text{SiMe}_3)_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, 2.535 Å)⁵⁵ and $\text{Cp}^*\text{NdCH}(\text{SiMe}_3)_2$ (2.517 Å).⁵⁶

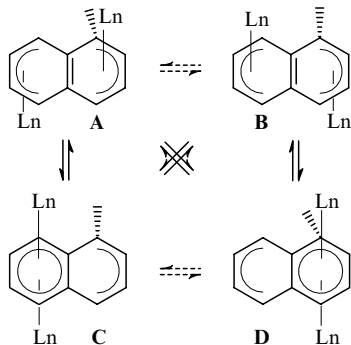
It was assumed^{46,57} that black insoluble finely dispersed products formed upon reduction of SmBr_3 and YbBr_3 with sodium naphthalenide are metallic lanthanides. However, there are strong grounds to believe that these reactions, like the analogous reactions with iodides, afforded naphthalene complexes of lanthanides. Apparently, the results of reduction of NdCl_3 with lithium naphthalenide were also misinterpreted.⁵⁸ Reinvestigation⁵⁹ of reduction of NdCl_3 with insufficient lithium in THF in the presence of naphthalene demonstrated that the reaction performed under these conditions gave rise to a mixture of naphthalene complexes with composition $[\text{NdCl}_2(\text{THF})_2\text{LiCl}]_n(\text{C}_{10}\text{H}_8)$ ($n = 4-7$) rather than divalent neodymium chloride $\text{NdCl}_2(\text{THF})_2$ as has been reported previously.⁶⁰

Binuclear complexes of the general formula $\{(\text{PhP}[\text{CH}_2.(\text{SiMe}_2)\text{N}(\text{SiMe}_2)\text{CH}_2]_2\text{PPh})\text{Ln}_2\text{Arn}\}$ (**19a–d**) [$\text{Arn} = \text{C}_{10}\text{H}_8$, $\text{Ln} = \text{Y}$ (**a**) or Lu (**b**); $\text{Arn} = \text{C}_{10}\text{H}_7\text{Me}$, $\text{Ln} = \text{Y}$ (**c**) or Lu (**d**)] containing the $\text{Ln}(\mu\text{-Arn})\text{Ln}$ group were prepared by the reactions of a mixture of potassium-intercalated graphite (KC_8) and naphthalene or 1-methylnaphthalene with the complex $\{(\text{PhP}[\text{CH}_2.(\text{SiMe}_2)\text{N}(\text{SiMe}_2)\text{CH}_2]_2\text{PPh})\text{YCl}_2\}$ (**9**) or its lutetium analogue.⁶¹ X-Ray diffraction analysis demonstrated that the fragments containing the phosphorus ligand bound to Y in the compound **19a**, like those in the complex $[\text{I}_2\text{La}(\text{THF})_3]_2(\mu\text{-C}_{10}\text{H}_8)$ (**17**), are located on the opposite sides of the bridging naphthalene ligand and are η^4 -bonded to the Y atoms. The shortest Y–C(1,2,3,4)(naphthalene) distances are 2.696, 2.684, 2.686 and 2.652 Å, respectively. The rings in the naphthalene ligand are folded along the $\text{C}(1)-\text{C}(4)$ and $\text{C}(5)-\text{C}(8)$ lines. According to the preliminary data, the lutetium analogue has a similar structure.



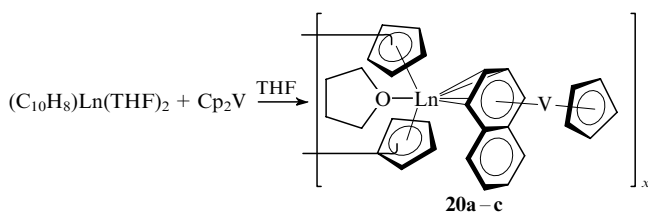
The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of all the four compounds are similar (the spectrum of the yttrium derivative has a doublet at

δ 21, $^1J_{\text{YP}} = 60$ Hz), which is indicative of the equivalence of the phosphorus ligands. Based on this fact, it was suggested⁶¹ that intramolecular migration of the $\{\text{PhP}[\text{CH}_2(\text{SiMe}_2)\text{N}(\text{SiMe}_2)\text{CH}_2]_2\text{PPh}\}\text{Ln}$ moieties between the naphthalene rings (structures **A–D**) occurs in solution. Apparently, the moieties migrate independently and, as a consequence, **A** is converted into **B** through the intermediates **C** and **D**.



R = H, Me; Ln = Y, Lu.

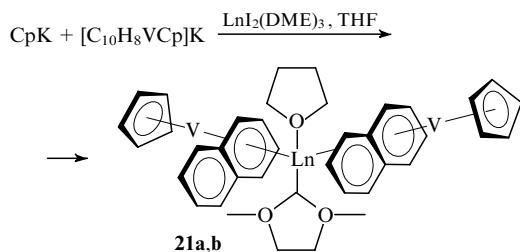
The lanthanide complexes $[\text{CpLn}(\text{THF})(\mu\text{-}\eta^4\text{:}\eta^6\text{-C}_{10}\text{H}_8)\text{VCp}]_x$ (**20a–c**) containing the bridging naphthalene ligand were prepared by the reactions of naphthalenytytterbium, -europium or -samarium with vanadocene.^{62,63}



Ln = Sm (**a**), Eu (**b**), Yb (**c**).

According to the data of ESR spectroscopy and magnetic measurements, the bridging naphthalene ligand in the complexes **20a–c** is neutral and the negative charge is located at the vanadium atom as a result of which the latter becomes formally zero-valent. Compounds of this type can be considered as dicyclopentadienyl complexes of lanthanides in which one of the cyclopentadienyl anions is coordinated to the metal atom through the neutral $(\text{C}_{10}\text{H}_8)\text{V}$ group.

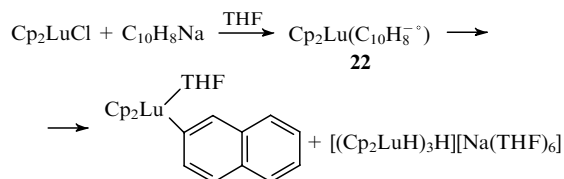
Analogous lanthanide–vanadium complexes $[\text{CpV}(\mu\text{-}\eta^6\text{:}\eta^6\text{-C}_{10}\text{H}_8)_2\text{Ln}(\text{THF})(\text{DME})]$ (**21**) were synthesised in THF by the reactions of samarium or europium diiodides with cyclopentadienylnaphthalenevanadium anions prepared *in situ*.⁶³ The reactions in hexane gave rise to monomeric complexes in which the rare-earth atom is coordinated to two $\text{CpV}(\text{C}_{10}\text{H}_8)$ units.



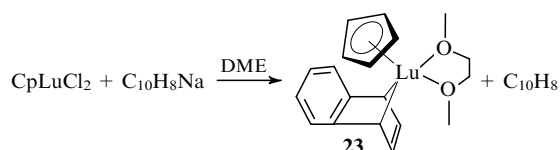
Ln = Sm (**a**), Eu (**b**).

The naphthalene ligands in the complexes **20** and **21** are planar. The $\text{Ln}–\text{C}(\text{naphthalene})$ bond lengths in the complex **20b** [$\text{Eu}–\text{C}(\alpha)$, 2.828 and 2.869 Å; $\text{Eu}–\text{C}(\beta)$, 3.037 and 3.098 Å] are indicative of η^4 -interaction in the $\text{CpLn}(\text{C}_{10}\text{H}_8)\text{VCp}$ moieties. In the quadruple-decker compound **21b**, the $\text{Eu}–\text{C}$ bond lengths are in the range of 2.872–3.084 Å, *i.e.*, η^6 -coordination occurs in the $(\text{C}_{10}\text{H}_8)\text{Eu}(\text{C}_{10}\text{H}_8)$ moieties.

The reaction of lithium naphthalenide with Cp_2LuCl proceeded through another pathway. In this case, the resulting (apparently, unstable) radical-anionic intermediate $\text{Cp}_2\text{Lu}(\text{C}_{10}\text{H}_8^{\cdot-})$ (**22**) underwent rapid conversions involving metallation of naphthalene and formation of hydride and naphthyl derivatives.⁶⁴



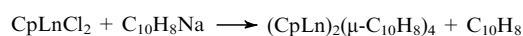
Reduction of CpLuCl_2 with sodium naphthalenide afforded the mononuclear complex $(\eta^5\text{-C}_5\text{H}_5)\text{Lu}(\text{C}_{10}\text{H}_8)(\text{DME})$ (**23**).⁶⁵



The molecular geometry of the complex is indicative of the σ -character of the bond between the lutetium atom and the naphthalene ligand whose coordinated ring loses aromaticity.

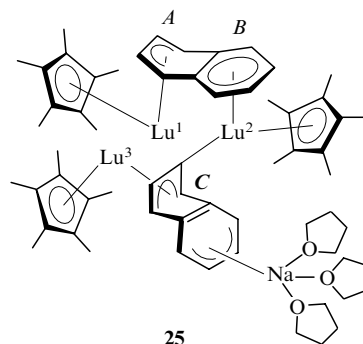
The $\text{Lu}–\text{C}(\alpha)$ bond lengths (2.406 and 2.397 Å) are comparable with the $\text{Lu}–\text{C}$ σ -bond lengths in the complexes $\text{Cp}_2\text{LuBu}^t(\text{THF})$ (2.47 Å)⁶⁶ and $\text{Cp}_2\text{LuCH}_2\text{SiMe}_3(\text{THF})$ (2.376 Å).⁶⁷ The $\text{Lu}–\text{C}(\beta)$ bond lengths (2.579 and 2.562 Å) are close to the $\text{Lu}–\text{C}(\text{Cp})$ bond lengths (2.65 Å), which suggests the presence of additional π -interaction of the lutetium atom with the double bond (1.36 Å) between the $\text{C}(\beta)$ atoms of the coordinated ring. The folding angle in the coordinated ring is 31.5°. Therefore, the bond between the naphthalene ligand and the metal atom in this case may be characterised as $2\eta^1\text{:}\eta^2(2\sigma,\pi)$ interaction.^{64,65,68} Analogous Y, Gd, Er and Tm complexes were also prepared.⁶⁹

In the reactions with $\text{C}_{10}\text{H}_8\text{Na}$ performed under comparable conditions, lanthanide derivatives characterised by lower potentials of $\text{Ln}(\text{II})/\text{Ln}(\text{III})$ transitions (such as Sm and Yb) were reduced to form the binuclear $\text{Ln}(\text{II})$ complexes containing the bridging naphthalene group, *viz.*, $(\text{CpLn})_2(\mu\text{-C}_{10}\text{H}_8)_4$ (**24**).⁶⁹



Ln = Sm, Yb.

The reaction with the use of the pentamethylcyclopentadienyl derivative of lutetium, Cp^*LuCl_2 , as the starting compound yielded the diamagnetic ate-cluster $\{[(\text{Cp}^*\text{Lu})_3(\text{C}_{10}\text{H}_8)(\text{C}_{10}\text{H}_7)]\cdot[\text{Na}(\text{THF})_3]\}^{2+}$ (**25**) whose trinuclear cation contains the naphthalene dianion and the naphthyl group with a charge of -3 .⁷⁰



The naphthalene dianion, which is not coordinated to the metal atoms, represents the anionic moiety of the complex. The ring *A* of one of the naphthalene ligands in the cationic moiety is η^4 -bonded to the $\text{Lu}(1)$ atom. As in the complex **23**, the $\text{Lu}–\text{C}$

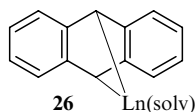
bond lengths of this fragment in **25** [Lu–C(α), 2.58 and 2.60 Å; Lu–C(β), 2.67 and 2.77 Å] and the folding angle along the C(α)–C(α) line (the dihedral angle is 172.5°) correspond to $2\eta^1 : \eta^2$ -interaction. The *B* ring remains planar and is η^6 -bonded to the Lu(2) atom (the Lu–C bond lengths are in the range of 2.61–2.88 Å). The $2\eta^1 : \eta^2$ -interaction is most pronounced in the Lu(3)–C₁₀H₇ group. In this case, the dihedral angle along the C(α) line is 142.5°. The Lu(3)–C(α,β) distances are 2.44, 2.47, 2.54, and 2.59 Å, respectively. The naphthyl ring *C* is σ -bonded to the Lu(2) atom. The short Lu(1)–ring *C* (2.81 Å) and Lu(3)–ring *A* (2.72 Å) distances are, apparently, indicative of some degree of bonding in these fragments. It is not inconceivable that the anionic cluster contains a bridging proton bound to the Lu(1) and Lu(2) atoms. However, the presence of this proton has not been unambiguously established.

It was reported⁷¹ that thin films of cerium and europium readily reacted with naphthalene in diethyl or dipropyl ethers at room temperature to form colourless solutions. Based on the spectral characteristics, it was concluded that pale-brown substances obtained after removal of the solvent and excess naphthalene are bis(naphthalene) π -complexes of zero-valent lanthanide of the bis(naphthalene)chromium type. However, this conclusion is in contradiction with the following facts: the products are pale in colour, which is untypical of neutral and charged arene complexes; under these conditions, naphthalene does not react with other lanthanides (Pr, Nd, Gd, Tb, Dy, Ho or Er); the reaction does not proceed in THF; the reaction with anthracene proceeds more slowly than that with naphthalene.

The reaction of acenaphthylene with permethylsamarocene readily proceeded in benzene giving rise to a dark-blue compound. According to the data of NMR and IR spectroscopy and elemental analysis, the compound can be described by the chemical formula (Cp^{*}Sm)₂(C₁₂H₈).⁷² The structure of the product was not established.

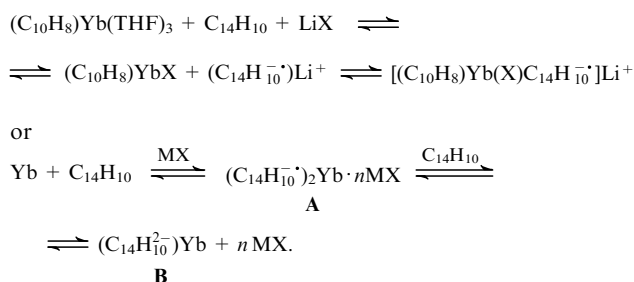
IV. Complexes with anthracene

Anthracene which possesses the higher electron affinity than naphthalene forms complexes with lanthanides in the direct reactions with ytterbium, samarium and cerium activated with diiodoethane.^{73–75} Attempts to isolate these complexes in an individual state failed. However, structure **26** was assigned to the resulting complexes by reasoning from the products of reactions with MeOD, MeI and Me₃SiCl.



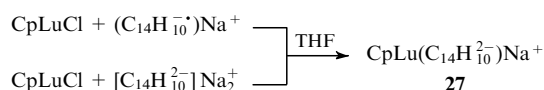
A film of metallic ytterbium prepared by concentrating a solution of the metal in liquid ammonia also reacted with anthracene in the presence of LiCl, NaBr, LiI, KI or Bu₄NI.⁷⁶ The authors believed that the reactions gave rise to complexes containing the anthracene radical anion with composition Yb(C₁₄H₁₀^{•−})₂·*n*MX. However, attempts to identify the reaction products were also unsuccessful. After washing of the substance with benzene, a violet powder containing the anthracene dianion, ytterbium and NaI in a ratio of 1 : 1 : 6 was obtained.

Anthracene complexes were prepared by the reactions of anthracene with naphthaleneytterbium in THF in the presence of alkali metal halides or by the reaction of YbI₂ with C₁₄H₁₀Na.^{40, 77} These complexes were isolated as black insoluble powders, which are similar in properties to naphthalene analogues. ESR spectral studies of these compounds and their hydrolysis products suggested the existence of an equilibrium between the radical-anionic (**A**) and dianionic (**B**) forms, with the latter predominating:

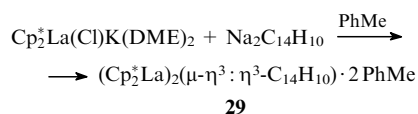
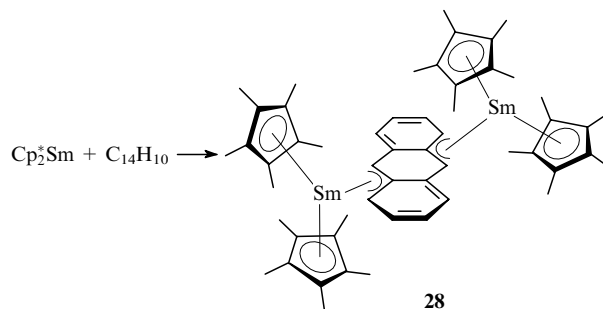


Since the resulting complexes are poorly soluble, their high-quality crystals were not prepared and the structures could not be established by X-ray diffraction analysis. However, analogous investigations were successfully performed by the use of cyclopentadienyllanthanide derivatives. It appeared that rare-earth metals form two types of anthracene complexes through addition at either an edge or a plane; however, the arene ligand in both cases carries a negative charge –2.

The reaction of CpLuCl with the dianion or two radical anions of anthracene gave rise to heterobimetallic ate-complex **27** containing the anthracene dianion.⁷⁸

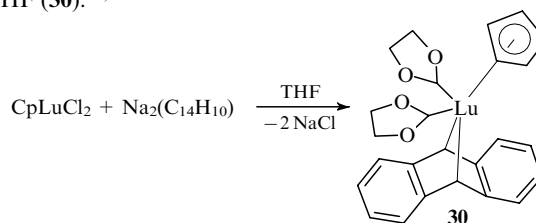


Neutral complexes of samarium (Cp^{*}Sm)₂(μ - $\eta^3 : \eta^3$ -C₁₄H₁₀) (**28**) and lanthanum (Cp^{*}La)₂(μ - $\eta^3 : \eta^3$ -C₁₄H₁₀)·2PhMe (**29**) with the anthracene dianion were prepared by oxidative addition of decamethylsamarocene to anthracene⁷² or by metathesis of the lanthanum potassium complex with disodium anthracene.⁷⁹



Both products are structurally similar. The planar anthracene dianion is $\eta^3 : \eta^3$ -bonded to two Cp^{*}Ln units located on the opposite sides of its plane. Apparently, the product of the reaction of Cp^{*}Sm with 9-methylanthracene, *viz.*, (Cp^{*}Sm)₂C₁₅H₁₂, has an analogous structure.⁷²

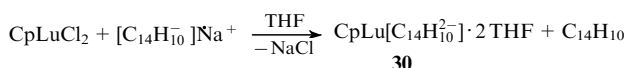
The reaction of C₁₄H₁₀^{2−} with CpLuCl₂ afforded a complex with different composition and structure, *viz.*, CpLu(C₁₄H₁₀^{2−})·2THF (**30**).^{80, 81}



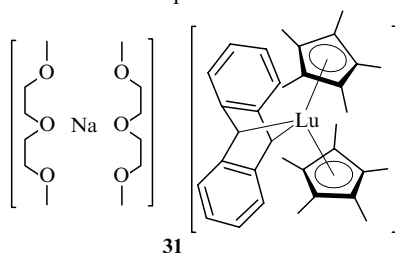
In the complex **30**, the character of the bond between the Lu atom and the arene ligand is analogous to that observed in the complex **23**, *i.e.*, it can be interpreted as σ, σ -interaction although

the Lu–C(9,10) distances (2.44 and 2.45 Å, respectively) are somewhat longer than the analogous contacts in the naphthalene derivative **23**, but are substantially shorter than those in the binuclear anthracene compound (2.683, 2.850 and 2.882 Å). The folding angle of the anthracene molecule along the C(9)–C(10) line is 38.7° (29.9° for the second symmetrically independent molecule in the crystal).

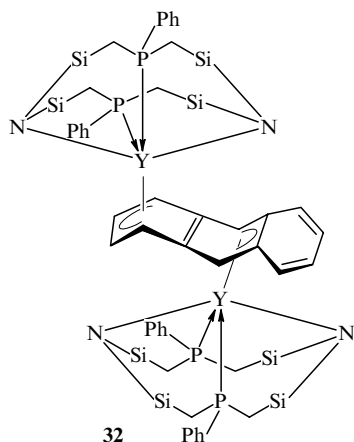
The complex **30** containing the anthracene dianion was also synthesised by the reaction of CpLuCl₂ with the anthracene radical anion. In this case, free anthracene was detected in the reaction mixture.^{80,81}



Unlike the lanthanum and samarium complexes, lutetium dicyclopentadienyl chloride gave the ate-complex [CpLu(C₁₄H₁₀²⁻)]·[Na⁺(THF)] in the reactions both with C₁₄H₁₀^{·-} and C₁₄H₁₀²⁻.⁸¹ The replacement of coordinated THF by diglyme afforded complex **31**. The authors managed to grow perfect crystals of **31** and to establish its structure by X-ray diffraction analysis.⁸¹ It appeared that the character of the bond between anthracene and the lanthanide atom in this compound is similar to that in the complexes CpLu(C₁₀H₈)(DME) (**23**) and CpLu(C₁₄H₁₀²⁻) (**30**). The arene ligand is folded along the C(9)–C(10) line (the dihedral angle is 40.1°). The shortest distances between the anthracene ligand and the lutetium atom [Lu–C(9,10) are 2.473 and 2.482 Å, respectively] are only 0.03 Å larger than the corresponding distances in the complex **30**.



The reaction of the aminophosphine yttrium complex **9** with anthracene in the presence of KC₈ yielded the binuclear complex ((PhP[CH₂(SiMe₂)N(SiMe₂)CH₂]₂PPh)₂(μ-C₁₄H₁₀)) (**32**). The latter, like the anthracene derivatives **30** and **31**, contains the C₁₄H₁₀²⁻ dianion.⁶¹ The metal atoms in the compound **32** are located on the opposite sides of the aromatic ligand and are η⁴-bonded to the central ring and one terminal ring.

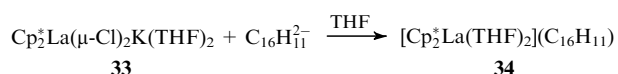


The coordinated rings are folded along the C(1)–C(4) and C(9)–C(10) lines. The shortest Y–C distances (the average values are 2.694 and 2.751 Å) are virtually identical to the corresponding distances in the naphthalene analogue **19a**. Based on the data of ¹H and ³¹P{¹H} NMR spectroscopy, it was assumed⁶¹ that in solution the metal-containing moieties in the

complex **32**, as those in the naphthalene derivative **19a**, migrate along the arene plane. It is significant that intermolecular migration of the {PhP[CH₂(SiMe₂)N(SiMe₂)CH₂]₂PPh}Ln moieties in the anthracene complexes or in mixtures of anthracene and naphthalene analogues does not occur. This is evidence that the complexes do not dissociate in solution in spite of the ionic character of the Ln–Arn bond.

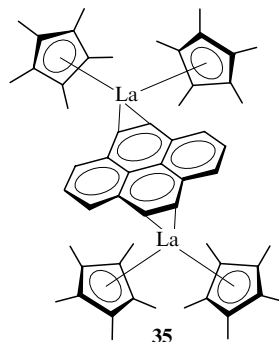
V. Pyrene and benzoanthracene derivatives

Pyrene can form three types of complexes with rare-earth metals.⁸² The reaction of Cp₂*La(μ-Cl)₂K(THF)₂ (**33**) with the pyrene dianion in THF afforded red crystals with composition [Cp₂*La(THF)₂](C₁₆H₁₁) (**34**) in low yield. The ¹H NMR spectrum of **34** has nine signals with equal intensities and one double-intensity signal (at δ 4.12). The authors believed⁸² that these signals are indicative of the presence of the hydropyrene anion C₁₆H₁₁⁻, which was, apparently, formed as a result of detachment of protons from the solvent.

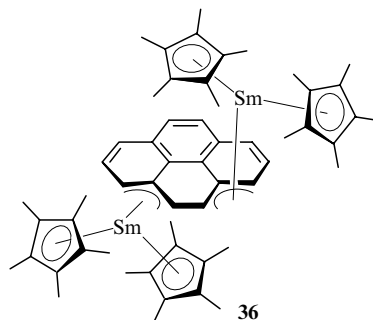


It was assumed⁸² that the [Cp₂*La(THF)₂]⁺ cation does not form a strong bond with the aromatic anion, *i.e.*, the complex in solution exists as a solvent-separated ion pair.

The reaction of the ate-complex **33** with pyrene and potassium in toluene taken in a ratio of 2:2:1 gave rise to black-green crystals. The NMR spectrum of these crystals corresponds to the binuclear complex (Cp₂*La)₂(μ-η²:η²-C₁₆H₁₀) (**35**). It was suggested⁸² that the Cp₂*La units in **35**, like those in the anthracene derivatives **29**, are located on the opposite side of the plane of the aromatic ligand and are bound to the opposite rings.



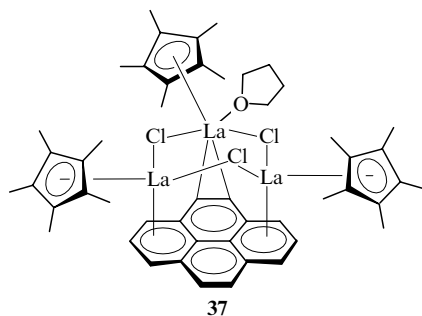
The samarium analogue (Cp₂*Sm)₂(μ-η³:η³-C₁₆H₁₀) (**36**), which was prepared by the reaction of free pyrene with Cp₂*Sm, differs in structure (according to the X-ray diffraction data) from **35**.⁷² Both metallocene moieties in **36** are coordinated at the edge of pyrene and are located above and below its plane, but they form three short contacts each with the adjacent rings rather than with the opposite rings.



The angles between the samarium atoms and the plane of the polycyclic ligand are 117° and 120°. The Sm–C distances are in the range of 2.660–2.806 Å, which is somewhat larger than the

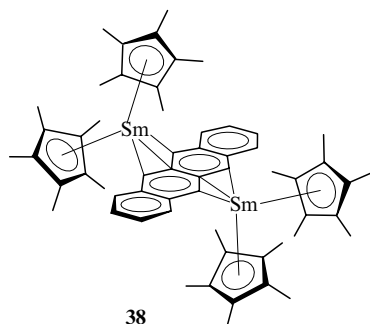
corresponding distances in the allylic complexes $\text{Cp}_2^*\text{Sm}(\eta^3\text{-CH}_2\text{CHCHR})$ (2.551–2.643 Å),⁸³ but are substantially shorter than the $\text{Sm}-\text{C}$ bonds in the arene chloroaluminate compounds $[\text{ArnSm}(\text{AlCl}_4)_3]$ (2.89–2.91 Å).^{5, 7, 11}

In the reaction with the use of the reagent ratio $\text{Cp}_2^*\text{Sm}:\text{pyrene}:\text{THF} = 3:3:1$ or in the reaction of pyrene and potassium with the monocyclopentadienyl complex $\text{Cp}^*\text{LaCl}(\mu\text{-Cl})_2\cdot\text{Li}(\text{THF})_2$, pyrene was reduced to the trianion yielding the red-violet trinuclear complex $(\text{Cp}^*\text{LaCl})_2[\text{Cp}^*\text{LaCl}(\text{THF})](\text{C}_{16}\text{H}_{10})$ (**37**).⁸² According to the X-ray diffraction data, all three Cp^*LaCl moieties are located above the plane of the pyrene ligand. Two of these moieties are η^6 -bonded to the arene ligand, whereas the third moiety containing an additional coordinated THF molecule forms only two short $\text{La}-\text{C}(\text{pyrene})$ contacts.



The lengths of the $\text{La}-\text{C}$ bonds with the participation of the η^6 -coordinated rings are in the range of 2.766–3.072 Å and the lengths of the $\text{La}-\text{C}$ bonds with the participation of the η^2 -coordinated rings are 2.823 and 2.841 Å, which are 0.1 Å larger than the corresponding contacts in the naphthalene complex $[\text{I}_2\text{La}(\text{THF})_3]_2(\mu\text{-C}_{10}\text{H}_8)$ (**14**).

2,3-Benzoanthracene, like pyrene, readily reacts with Cp_2^*Sm to give green crystals of the complex $(\text{Cp}_2^*\text{Sm})_2(\mu\text{-}\eta^3:\eta^3\text{-C}_{18}\text{H}_{12})$ (**38**),⁷² which is structurally similar to the pyrene complex **36**. Two Cp_2^*Sm fragments are coordinated at the edge of the arene ligand and are located on the opposite sides of its plane. The distance from the Sm atoms to this plane is 2.063 Å. Both metal atoms are bound to the same central ring. The $\text{Sm}-\text{C}(\text{Arn})$ bond lengths (2.688–2.828 Å) are similar to those in the pyrene analogue **36**.

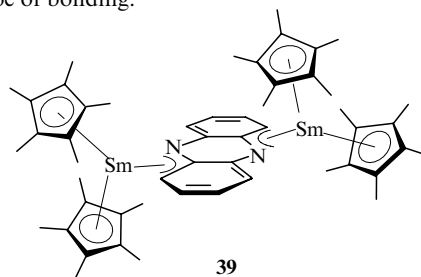


Interestingly, all permethylsamarocene complexes with arenes, unlike other arenelanthanides, are readily decomposed upon dissolution in THF to form $\text{Cp}_2^*\text{Sm}(\text{THF})_2$ and the corresponding polycyclic hydrocarbon.⁷² This lability of the $\text{Sm}-\text{Arn}$ bond may be evidence for its nonvalent character, *i.e.*, the formation of these derivatives is not accompanied by redox processes and the coordination complexes $[\text{Cp}_2^*\text{Sm}(\text{II})]_2(\text{Arn}^0)$ are formed. However, the ^1H and ^{13}C NMR spectra of the reaction products are unambiguously indicative of the change in the valence state of the metal atom from $\text{Sm}(\text{II})$ to $\text{Sm}(\text{III})$ in the course of the reaction and, consequently, the arene ligand in the complexes exists as the dianion. The $\text{Sm}-\text{Cp}^*$ distances in these complexes and their electronic spectra also correspond to trivalent samarium. The characteristic feature of the permethylsamarocene complexes with arenes is the allylic type of bonding between the arene ligand and the Cp_2^*Sm unit.⁷²

VI. Complexes with heterocyclic aromatic ligands

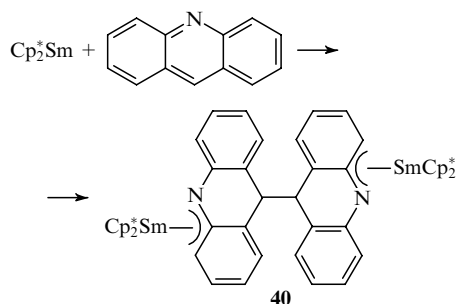
The great majority of complexes of rare-earth metals with heterocyclic aromatic ligands are formed through coordination interaction between the lone electron pair of the heteroelement and the Ln atom.¹ In these complexes, the ligands can be either neutral or charged (-1 or -2). The charges are localised primarily on heteroatoms. However, examples of compounds similar in nature to typical bisarene complexes are also available. One of them, *viz.*, $(2,4,6\text{-Bu}_3\text{C}_5\text{H}_2\text{N})_2\text{Sc}$, was prepared under conditions of the cryogenic synthesis.³ It was suggested that this compound contains the formally zero-valent scandium atom and the neutral *tert*-butyl-substituted pyridine ligands. The molecule was represented as a planar-parallel sandwich.

The reaction of Cp_2^*Sm with phenazine, like that with anthracene, afforded the binuclear complex $(\text{Cp}_2^*\text{Sm})_2(\mu\text{-}\eta^3:\eta^3\text{-C}_{12}\text{H}_8\text{N}_2)$ (**39**) in which the samarocene fragments are in the transoid orientation with respect to the $[\text{C}_{12}\text{H}_8\text{N}_2]^{2-}$ dianion.⁷² The presence of three short contacts between the samarium atoms and the phenazine ligand are indicative of the allylic type of bonding.



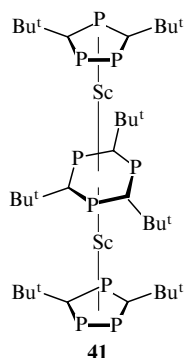
The $\text{Sm}-\text{N}$ bond length (2.360 Å) is slightly larger than the $\text{Sm}-\text{N}$ σ -bond length in the complex $\text{Cp}_2^*\text{SmN}(\text{SiMe}_3)_2$ (2.306 Å),⁸⁴ which is evidence for substantial localisation of the charge on the nitrogen atoms, as in the complexes of the $\text{Cp}_3\text{Ln}(\text{py})$ ¹ and $\text{Ln}(\text{bipy})_4$ types (bipy is 2,2'-bipyridyl).⁸⁵

The reaction of permethylsamarocene with acridine was accompanied by dimerisation of the latter to form a $\text{C}-\text{C}$ bond.⁷³



The character of the metal–arene bond in the complex **40** is analogous to that in the phenazine derivative, *i.e.*, corresponds to η^3 -interaction, with the $\text{Sm}-\text{N}$ component predominating.

Arene lanthanide complexes of an unusual type were prepared by cocondensation of vapours of scandium and *tert*-butylphosphoalkyne $\text{Bu}^t\text{C}\equiv\text{P}$ at 77 K.⁸⁶ The reaction was accompanied by cyclisation of the phosphoalkyne giving rise to two products, *viz.*, dark-violet scandocene $(\eta^5\text{-Bu}_3\text{C}_3\text{P}_2)_2\text{Sc}$ containing divalent scandium and the green triple-decker complex $[(\eta^5\text{-Bu}_3\text{C}_2\text{P}_3)\text{Sc}]_2$ (**41**) containing formally monovalent scandium. The valence states of the scandium atoms in both complexes were unambiguously established by UV and ESR spectroscopy and magnetic measurements. The structure of the triple-decker complex was confirmed by X-ray diffraction analysis.⁸⁷ The central six-membered ring in the complex **41** is located on a crystallographic mirror plane. All $\text{P}-\text{C}$ bond lengths in this ring have closely similar values (1.793–1.807 Å).

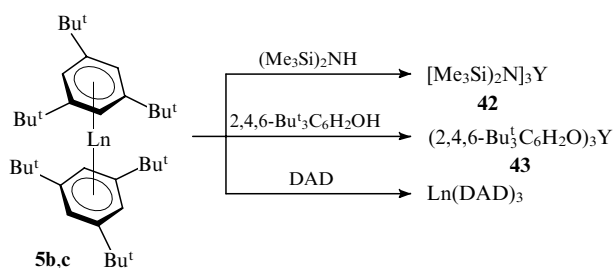


It is worthy of note the distance from Sc to the central ring in the compound **41** is noticeably shorter (1.787 Å) than the analogous distance in the bisarene complex $(\text{Bu}^t_3\text{C}_6\text{MeH}_2)_2\text{Sc}$ (1.983 Å).⁸⁷ In spite of the valence state +1 untypical of scandium, the compound **41** is quite stable and can be even sublimed *in vacuo* at 250 °C. The magnetic moment (3.98 μ_B) of **41** is somewhat smaller than the value calculated for four unpaired electrons, which was attributed to the presence of an orbital contribution.⁸⁷

VII. Reactivity of arene lanthanide complexes

The chemical properties of complexes of rare-earth metals with π -bonded arene ligands were studied primarily using naphthalene derivatives as examples. For compounds with other aromatic hydrocarbons, only the most common characteristics are known. All arene lanthanide complexes exist as dark-coloured solids, which are readily oxidised in air (often with ignition). It was found that bisarene complexes of formally zero-valent Sc, Y, Nd, Gd, Tb, Dy, Ho, Er and Lu are thermally stable under an inert atmosphere or *in vacuo*. Some of them can even be sublimed with insignificant decomposition at 100 °C (at 10^{-4} mm Hg). These complexes are readily soluble in aromatic and aliphatic hydrocarbons. Complexes with arene dianions are virtually insoluble.

The yttrium complex $(1,3,5\text{-Bu}^t_3\text{C}_6\text{H}_3)_2\text{Y}$ (**5b**) readily reacted with phenol, 2,4,6- $\text{Bu}^t_3\text{C}_6\text{H}_2\text{OH}$ and hexamethyldisilazane to form tri(aryloxyde) (**42**) and yttrium tris(trimethylsilyl)amide (**43**) in good yields. The reaction of the holmium complex **5c** with bi-*tert*-butyl-1,3-diazabuta-1,3-diene (DAD) also resulted in complete replacement of the arene ligands.³



Ln = Y (**b**), Ho (**c**); DAD = $\text{Bu}^t\text{N}=\text{CHCH}=\text{NBu}^t$.

All $(\text{Ar}_n)_2\text{Ln}$ complexes are efficient catalysts of ethylene polymerisation.

Naphthalene lanthanide complexes of all types exhibit very high reactivities with respect to many inorganic, organic and organometallic compounds. Essentially in all cases, these complexes act as strong reducing agents comparable in reducing ability to alkali metal naphthalenides. The reactions were carried out in THF or DME at room or lower temperature. Generally, the yields of the products many of which were characterised by X-ray diffraction studies are higher than 60%–70%. Hence, these reactions may be recommended as preparative (often the only

possible) procedures for the synthesis of organolanthanide compounds. The important advantage of these syntheses is the fact that the second product, *viz.*, naphthalene, is unreactive and can be readily separated from the target compound. The reactions with the participation of the complexes $(\text{C}_{10}\text{H}_8)\text{Ln}(\text{THF})_x$ are listed in Table 1.

The compounds $(\text{C}_{10}\text{H}_8)\text{Ln}(\text{THF})_x$ also exhibit high reactivity in catalytic processes. Thus the complex $(\text{C}_{10}\text{H}_8)\text{Yb}(\text{THF})_3$ catalyses hydrogenation of hex-1-ene, stilbene, isoprene and piperylene at room temperature under atmospheric pressure of H_2 yielding the corresponding hydrocarbons.⁴¹ Tolan was hydrogenated to form *trans*-stilbene and diphenylethane. In the presence of 1%–5% of $(\text{C}_{10}\text{H}_8)\text{Yb}(\text{THF})_3$, styrene, methyl methacrylate, ethyl acrylate, isoprene and piperylene formed polymers at room temperature.⁴⁸ The conversion reached 100% in several hours. Piperylene produced more than 80% of the *trans*-polymer, whereas polyisoprene was obtained as a mixture of virtually equal amounts of *cis* and *trans* forms. Naphthaleneytterbium catalyses polymerisation of epoxides and their reactions with CO_2 . In the latter case, a mixture of monomeric and polymeric alkyl carbonates was obtained.⁴⁸ It is interesting to note that naphthalene complexes of 'trivalent' lanthanides, which were not isolated in the individual state, appeared to be efficient catalysts of polymerisation of conjugated dienes.⁴³ The reactions of the latter [like that of $(\text{C}_{10}\text{H}_8\text{Tm})_2(\text{C}_{10}\text{H}_8)$] with cyclopentadiene afforded the corresponding Cp_3Ln in 15%–60% yield depending on the metal.^{52, 53}

It was found⁵⁸ that the products of the reaction of NdCl_3 with $\text{C}_{10}\text{H}_8\text{Li}$ (apparently, the reaction afforded naphthalene neodymium complexes rather than finely dispersed neodymium as has been suggested in Ref. 58) readily reacted with ketones and aldehydes to yield the corresponding diols or ethylene derivatives as a results of coupling of the substrate.

Generally, mixed-ligand complexes containing naphthalene as well as the iodine atom, the cyclopentadienyl substituent or the double-decker $\text{CpV}(\text{C}_{10}\text{H}_8)$ moiety bound to the rare-earth element react analogously to compounds of the $(\text{C}_{10}\text{H}_8)\text{Ln}(\text{THF})_3$ type, *i.e.*, the attack occurs primarily on the $(\text{C}_{10}\text{H}_8)\text{Ln}$ group. Due to the presence of the LnI or LnCp groups along with the $\text{Ln}(\text{C}_{10}\text{H}_8)$ moiety, these complexes are convenient starting compounds for the preparation of complexes of the RLnI or RLnCp types. The most typical reactions are given in Table 2.

The chemical properties of anthracene lanthanide complexes are analogous to the properties of their naphthalene analogues. However, the activities of the former are substantially lower. Thus the reactions of anthraceneytterbium with cyclopentadiene, fluorene, 9-*tert*-butylfluorene, tetraphenylpropene and 9-phenylxanthene in solutions afforded the corresponding anions, *i.e.*, the R_2Ln compounds apparently formed, but the reaction rates were low (from several days to weeks). Triphenylmethane did not enter into the reaction at all.⁷⁶ Deuterolysis of the complexes $(\text{C}_{14}\text{H}_{10})\text{Ln}(\text{THF})_x$ ($\text{Ln} = \text{Sm}$ or Yb) gave rise to 9,10-dideutero-9,10-dihydroanthracene,^{48, 74} whereas their reactions with MeI afforded a mixture of 9,10-dimethyl-9,10-dihydroanthracene (14%–20%), $\text{MeC}_{14}\text{H}_9$ (1%–4%) and 9,10-dihydroanthracene (13%–25%). It is noteworthy that attempts to alkylate naphthalene in the reactions of naphthaleneytterbium with different alkyl halides have not met with success. In all cases, only unsubstituted naphthalene was obtained.[‡]

For anthracene mixed-ligand complexes of lanthanides, only the reaction of $\text{CpLu}(\text{C}_{14}\text{H}_{10})(\text{THF})_2$ with iron pentacarbonyl giving rise to the heterobimetallic product with composition $[\text{CpLu}(\text{THF})]\text{Fe}(\text{CO})_4$ was reported.¹⁰⁶

‡ Unpublished data of the author of the present review.

Table 1. Reactions of the naphthalene complexes $(C_{10}H_8)Ln(B)_x$ ($Ln = Sm, Eu$ or Yb ; $B = THF$ or DME , $x = 2$ or 3).

Substrate	Products	Ref.
O_2	$Ln_2O_3 + C_{10}H_8$	48
H_2	$LnH_2 + C_{10}H_8$	88, 89
H_2O	$C_{10}H_{10} + Ln(OH)_3$	48
Bu^tOH	$(Bu^tO)_2Ln + C_{10}H_8$	see ^a
R_2NH [$R = Et, N(SiMe_3)_2$]	$(R_2N)_2Ln + C_{10}H_8 + C_{10}H_{10} + H_2$	48
CpH	$Cp_2Ln + C_{10}H_8 + H_2$	48
$IndH^b$	Ind_2Yb	see ^a
$FluH^c$	Flu_2Yb	see ^a
$CpCH_2CH_2OH$	$[(\eta^5-Cp)CH_2CH_2(\eta^1-O)]Yb(B) + C_{10}H_8 + H_2$	90
$CpCH_2CH(Me)OH$	$[(\eta^5-Cp)CH_2CH(Me)(\eta^1-O)]Yb(THF) + C_{10}H_8 + H_2$	90
$CpCH_2CH(CH_2OBu)CH_2OH$	$[(\eta^5-Cp)CH_2CH(CH_2OBu)CH_2(\eta^1-O)]Yb(THF) + C_{10}H_8 + H_2$	90
$CpSiMe_2NHBu^t$	$[(\eta^5-Cp)SiMe_2(\eta^1-NBu^t)]Yb(THF) + C_{10}H_8 + H_2$	90
$C_3Me_4HSiMe_2OSiMe_2OH$	$\{[(\eta^5-Cp)Si(Me_2)OSi(Me_2)(\eta^1-O)]Yb(THF)\}_2 + C_{10}H_8 + H_2$	91
$HC \equiv CH$	$LnC_2(THF)_x + C_{10}H_8 + H_2$	45
$PhC \equiv CH^d$	$(PhCH=CHCH=CHPh)Ln(DME)_2 + C_{10}H_8$	92
Ph_2Hg^e	$Ph_2Yb(THF)(\mu-Ph)_3Yb(THF)_3 + Ph_3Yb + Hg + C_{10}H_8$	93
Ph_3GeH^e	$(Ph_3Ge)_2Yb(THF)_4 + C_{10}H_8 (Ph_3Ge)_2Eu(DME)_3 + C_{10}H_8$	88, 94
Ph_4Sn^e	$Ph_3SnYb(THF)(\mu-Ph)_3Yb(THF)_3 + (Ph_3Sn)_2Yb(THF)_4 + C_{10}H_8$	95, 96
Ph_6Sn_2 (see ^e)	$(Ph_3Sn)_2Yb(THF)_4 + C_{10}H_8$	96
Cp_2V^d	$CpVC_{10}H_8VCp$ $[CpLn(THF)C_{10}H_8VCp]_n$	62, 63, 97
Cp_2Ni^e	Cp_2Yb	97
Cp_2Co^e	Cp_2Yb	97
Cp_2Cr^e	$Cp_2Yb + (C_{10}H_8)_2Cr$	97
DAD^e	$Yb(DAD)_3 + C_{10}H_8$	98
$bipy^{e,f}$	$[Yb(\mu_2-bipy)(THF)_3]_3$	99
$PhN=NPh^e$	$[Yb_4(\mu_2-\eta^2:\eta^2-Ph_2N_2)_4(\mu_3-PhN)_2(THF)_4]$	39
see ^f	$[Sm_4(\mu_2-\eta^2:\eta^2-Ph_2N_2)_4(\mu_3-PhN)_2(THF)_6]$	47
$PhC \equiv CPh^h$	$[CpLu(DME)]_2[1,1-\mu-4,4-\mu-PhCC(Ph)=(Ph)CCPh] + C_{10}H_8$	100
S_8 (see ^f)	$SmS(THF) + C_{10}H_8$	101
RX ($R = Ph, C_6F_5, X = Br, I$)	$RLnX$ (Sm, Yb)	46
RX ($R = Ph, 4-BrC_6H_4, \text{thiophene}, X = Br$)	$RLnX$ (Sm, Yb)	57
Ph_2CO (H^+)	$(Ph_2COH)_2$	48
$PhCHO$ (H^+)	$(PhCHOH)_2$	48
cyclopropane (H^+)	$HOCH_2(CH_2)_2CH_2OH + C_{10}H_8$	48
CO_2	$C_{10}H_8(COOH)_2$	48
CO	$C_{10}H_8(COOH)_2$	48

^a Unpublished data of the author of the present review; ^b Ind is 9-indenyl; ^c Flu is 9-fluorenyl; ^d for Eu and Yb; ^e for Yb; ^f for Sm; ^g for Lu.

Table 2. Reactions of the naphthalene mixed-ligand lanthanide complexes.

Complex	Substrate	Products	Ref.
$[LaI_2(bipy)_2(THF)_3]_2[C_{10}H_8]$	bipy	$LaI_2(bipy)_2(DME) + C_{10}H_8$	102
	bipy	$LaI_2(bipy)(DME)_2 + C_{10}H_8$	102
$[YbI(DME)_2]_2(C_{10}H_8)$	bipy	$YbI(bipy)(DME)_2$	103
$Cp^*Lu(C_{10}H_8)(DME)$	C_{60}	$Cp^*Lu(C_{60})(DME)$	104
$CpLu(C_{10}H_8)(DME)$	H_2O	$Lu(OH)_3 + C_{10}H_{10} + CpH$	65
	O_2	$Lu_2O_3 + C_{10}H_8$	65
	CpH	$Cp_3Lu + C_{10}H_{10} + C_{10}H_8 + H_2$	65
	$PhC \equiv CPh$	$[CpLu(DME)]_2[1,1-\mu-4,4-\mu-PhCC(Ph)=(Ph)CCPh] + C_{10}H_8$	99
$CpLu(C_{10}H_8)(THF)_2$	Ph_2N_2	$[CpLu(THF)]_2(Ph_2N_2)$	99
$(C_{10}H_8)[LnI(DME)_2]_2$ (see ^a)	$PhC \equiv CH$	$[PhC \equiv CLnI(DME)_2]_2 + C_{10}H_8 + H_2$	95
$(C_{10}H_8)[EuI(DME)_2]_2$	Ph_3GeH	$Ph_3GeEuI(DME)_2 + C_{10}H_8 + H_2$	97
$[CpV(C_{10}H_8)YbCp(THF)]_n$	H_2O	$CpYbOH(THF)_2 + CpVC_{10}H_8$	105
	CO	$Cp_2Yb + CpVC_{10}H_8$	105
	CO_2	$Cp_2Yb + CpVC_{10}H_8$	105
	$Cr(CO)_6$	$Cp_2Yb + CpVC_{10}H_8 + Cp_2V + CpVC_{10}H_8VCp + C_{10}H_8$	105
	$CpTi$	$Cp_2Yb + CpVC_{10}H_8$	105
	Ph_2N_2	$[CpYb(THF)]_2(Ph_2N_2)_2 + CpVC_{10}H_8$	105

^a For Eu and Yb.

VIII. Conclusion

Based on analysis of the available data, the characteristic features of complexes of rare-earth metals with π -bonded arene ligands were revealed. First, it should be noted that these compounds exist in the two major forms, *viz.*, with neutral arene or with the arene dianion. Forms with arene carrying a charge -1 or -3 are untypical of these complexes. Apparently, these forms can be obtained and exist only under particular conditions. It should be noted that the tendency of lanthanides to form complexes of the $[\text{Ln}]^{2+}[\text{L}]^{2-}$ type even in the presence of the free uncharged ligand is also observed in the case of other ligands (such as bipy[§] or DAD) exhibiting polyvalence.¹⁰⁷ The mode of bonding of lanthanide with arene ligands can vary from η^2 to η^6 . The Ln atom can be coordinated both at the plane of the arene ligand and at its edge. The character of the Ln–Arn bond in complexes with neutral arene and formally zero-valent lanthanide is similar to the character of the metal–arene bond in complexes of *d* metals, *i.e.*, the bond is determined by back donation of the electron density from the occupied d_{xy} and $d_{x^2-y^2}$ orbitals of lanthanide to the unoccupied π -orbitals of arene. In compounds with neutral ligands coordinated to the Ln^{3+} cation {complexes of the $(\text{Arn})\text{Ln}[(\mu\text{-Cl})_2\text{AlCl}_2]_3$ or $\text{Ln}(\text{OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_3$ types}, the *d* orbitals of the metal atoms are unoccupied and interactions occur, apparently, through donation of the electron density from the π -orbitals of the arene ligand to the unoccupied orbitals of the metal atom. The metal–arene bonds in these compounds are substantially weaker as evidenced by the noticeably elongated Ln–C(arene) bonds. In complexes containing Ln^{2+} , $(\text{XLn})^{2+}$ or $(\text{X}_2\text{Ln})^+$ cations and the arene dianion (naphthalene lanthanide complexes and related derivatives) bonding occurs, apparently primarily through Coulomb interactions between the positively and negatively charged moieties of the molecule. However, the structures of the complexes and the fact that these complexes contain the shortest Ln–C(arene) bonds of all arene lanthanide complexes are indicative of the presence of the second bonding component, *viz.*, of donation of electron density from the π -orbitals of arene to the unoccupied orbitals of the metal atom. In spite of the high (judging from the geometric parameters of the molecules) energy of the metal–arene bond, naphthalene lanthanide complexes exhibit very high reactivity. At the same time, these complexes are readily accessible owing to which they show promise as a source of lanthanides or lanthanide-containing fragments in the synthesis of other derivatives of rare-earth metals.

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Solid-phase synthesis of oligosaccharides and glycoconjugates

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Abstract. The use of polymeric supports for directed regiospecific assembly of oligosaccharides, glycopeptides and phosphoglycans is considered. In some cases, synthesis of oligosaccharides on supports is more efficient than the corresponding synthesis in solution, although this cannot still compare favourably with the latter. Examples of successful solid-phase syntheses of complex oligosaccharides and glycoconjugates are given. Special emphasis is laid on the choice of optimum supports, linkers and glycosylation methods. The bibliography includes 105 references.

I. Introduction

The explosive development of molecular biology is closely connected with recent advances in the chemistry and biochemistry of biopolymers including the development of efficient techniques for their targeted chemical synthesis. The recently developed approaches to the synthesis of biopolymers are based on essentially new principles for elongation of the polymeric chains including their assembly on polymeric supports.

This method was first employed by Merrifield for the synthesis of peptides.¹ After solution of numerous methodological problems, this protocol, which is sometimes improperly referred to as 'solid-phase synthesis', was successfully automated and became the main routine procedure in peptide synthesis.

An enormous body of experimental evidence published in the past two-three decades point to the prominent role of biopolymers, such as polysaccharides and glycoconjugates (glycoproteins, glycolipids) in vital processes. These polymers are indispensable participants in many biological processes (*e.g.*, antigen–antibody, enzyme–substrate and ligand–receptor interactions) as well as in some other interactions of carbohydrates with proteins.^{2,3}

The first attempts aimed at synthesising oligosaccharide chains on solid supports were undertaken in the early 1970's;^{4,5} however, it became clear that rapid progress in this area was hardly possible, since chemical synthesis of oligosaccharides with

a strictly determined sequence of monomeric units presented a serious problem due to the polyfunctionality of monosaccharides and the stereochemical ambiguity of intermonomeric glycosidic bond formation.

At present, synthesis of oligosaccharides on polymeric supports still cannot compete with the classical synthesis in solution, but its development is in progress and the methodology is improved. This is associated with the fact that in many cases syntheses on supports are more advantageous. Numerous examples of successful application of the solid-phase approach in the synthesis of complex oligosaccharides and glycoconjugates are currently known.

A vast body of experimental material accumulated thus far highlights the major problems and advances in solid-phase synthesis of carbohydrate-containing compounds and allows estimation of its possible application for realistic syntheses. It seems therefore expedient to sum up these data in order to inform all those who are concerned with this subject about the potential of the method and the problems it may involve.

The review covers the publications appearing up to 1999 inclusive.

II. The methodology of synthesis of oligosaccharide chains on solid supports

The synthesis of oligosaccharides on solid supports includes immobilisation of the first unit from which elongation of the oligosaccharide chain begins on a specially selected optimum support followed by elongation of the oligosaccharide chain using specific methods for the formation of interglycosidic linkages (*viz.*, by glycosylation) and removal of the oligosaccharide molecules thus synthesised from the polymeric support without any sacrifice of their structures. The peculiarity of carbohydrate chemistry is manifested in all steps of the solid-phase oligosaccharide synthesis, which makes it different from peptide and nucleotide syntheses.

1. Supports

Oligosaccharide syntheses are carried out both on insoluble solid supports and on soluble polymers. In the former case, the reaction proceeds in heterogeneous media, in the latter case, in homogeneous media.

The obvious advantage of insoluble solid supports is that the isolation and purification of the reaction products after each step is achieved by simple filtration and washing with a solvent.

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Furthermore, the reaction rate can be increased if one of the reagents, which can be regenerated following the reaction, is taken in a large excess. The main disadvantage of insoluble supports is that the reaction occurs on a solid surface, which hampers the access of the reagent to the reaction centre and poses additional difficulties in regulation of regio- and stereoselectivity of the reaction.

Syntheses of oligosaccharide chains anchored to soluble polymeric supports are partly devoid of this drawback but purification of the reaction product becomes more difficult. In this case, the polymer-bound reaction product has to be precipitated by addition of another solvent and purified by repeated precipitations. The use of an excess of a reagent for acceleration of the reaction is also undesirable, since in this case its complete removal, which is necessary to ensure the desired sequence of the monomeric units in the 'growing' chain, faces difficulties. On the other hand, glycosylation in a homogeneous medium offers better opportunities for regulation of regio- and stereospecificity of the reaction.

Currently, both types of supports for the synthesis of oligosaccharides are employed; however, synthesis on soluble polymers (especially, synthesis of glycoconjugates) has acquired ever increasing importance in recent years.

a. Insoluble solid supports

The efficiency of solid-phase synthesis strongly depends on the physicochemical properties of solid supports, such as porosity and swelling capacity in different solvents. These characteristics are very important, since they determine the accessibility of immobilised molecules to the reagent present in the solution. The number of moles of the first monomeric unit from which elongation of the chain begins, which can be immobilised per g of the polymeric support (the so-called 'loading'), is yet another factor of considerable practical importance.

In the early period of solid-phase oligosaccharide synthesis, polystyrene-based resins prepared by copolymerisation of styrene with *p*-divinylbenzene were predominantly employed. Commercial resins of this type are now available as powders with particles having spherical shapes ('beads') and differing in the degree of cross-linking, porosity, swelling capacity and particle size.[†] Modified polystyrenes containing reactive chloromethyl (Merrifield's polymer), phenolic hydroxy groups,⁷ mercaptomethyl,⁸ sulfonylmethyl,⁹ diphenyl- and diisopropylchlorosilyl,¹⁰ (3-mercaptopropyl)oxy(thio)methyl^{11,12} and some other groups are most commonly used as supports. The choice of a particular polystyrene resin as a solid support is determined by the strategy of a realistic synthesis, the mode of attachment of the first monomer to the solid phase and the structure of the linker. Sometimes, the role of a linker is played by the functional group of the polystyrene resin.

A main disadvantage of polystyrene resins used in solid-phase oligosaccharide synthesis is their poor compatibility with biomolecules. For example, the yields of oligosaccharides in enzymic solid-phase synthesis catalysed by glycosyl transferases were low to such an extent that this method had to be abandoned as being impractical.

Attempts were undertaken aimed at using polyacrylamide gels as supports. Prior to the use, the gels were modified, *e.g.*, by incorporation of aminoethyl groups.¹³

Controlled-pore glasses (CPG) with a modified surface, *e.g.*, with grafted 3-aminopropyl groups serving to attach the first monomer (see, *e.g.*, Refs 14 and 15), are currently employed with increasing frequency. The surface of CPG-based supports can be modified by silanisation with prior zirconation.¹⁶ The use of CPG has a number of advantages, since they offer broad opportunities in the selection of supports of desired porosity and allow appropriate modification of the surface.

[†] A brief survey of polymeric substrates for solid-phase syntheses is given in Ref. 6.

b. Soluble supports

These types of supports have currently acquired wide popularity. The simplest soluble support is polyethylene glycol (PEG) ($M_r \sim 5,000$ Da) in which one of the terminal hydroxy groups is methylated and the other one is free and serves to immobilise the first monomer (either directly or through a linker).¹⁷ Commercially available PEG is easily soluble in many solvents.

Polymers of a hybrid type, containing both hydrophobic and hydrophilic fragments, have received considerable attention in the last few years. The synthesis on such materials is carried out in a 'micromedium', *i.e.*, under conditions mimicking those of a homogenous reaction, and at the same time allows easy isolation of the reaction products after each step. These polymers include a copolymer of acrylamide or its N-substituted derivatives with polyethylene glycol (PEGA) possessing terminal amino groups¹⁸ and a copolymer of polystyrene with polyethylene glycol (Tentagel).¹⁹ Other more sophisticated copolymers are also used and will be discussed below.

2. Linkers

In solid-phase syntheses of oligosaccharides, the first monomer is usually attached to the support through a bifunctional group (the so-called linker) rather than directly. The linker serves both to bind the monomer to the polymer and to make the monomer and the growing chain remote from the support in order to minimise the influence of the solid surface on the course of the reaction. The latter circumstance is especially important, since heterogeneity of the medium has a specific, sometimes rather obscure effect on the stereochemistry of the newly formed glycosidic linkage.

In deciding upon a linker, allowance should be made for the possibility of selective cleavage of one of its linkages in the release of the oligosaccharide synthesised from the solid support without affecting labile glycosidic bonds.

In early oligosaccharide syntheses, the first monosaccharide was immobilised on chloromethyl-polystyrene without linkers. However, later the use of linkers differing in structures and chemical properties became common practice.

It should be noted that in contrast with the conventional solid-phase peptide and oligonucleotide syntheses, diverse linkers are utilised in solid-phase syntheses of carbohydrates. The choice of a suitable linker for a realistic purpose is an indispensable step in the design of a synthesis. In the synthesis of glycopeptides, the peptide chain is often used as a linker which also removes the growing carbohydrate chain from the surface of the support. A more detailed description of linkers will be given further below in relation to particular syntheses.

3. Elongation of the oligosaccharide chain

This step is crucial in oligosaccharide synthesis, therefore the choice of a method for the formation of glycosidic bonds between the monosaccharides (*i.e.*, method of glycosylation) determines the overall strategy of the synthesis. The predetermined sequence of monosaccharides necessitates that the formation of glycosidic linkages is strictly regio- and stereospecific. A prerequisite for the preparation of homogeneous oligosaccharides with a predetermined structure, which should not require any additional purification (it is this that makes solid-phase synthesis advantageous in comparison with the classical synthesis in solution), is that the yields were close to quantitative in all steps. The lack of a versatile glycosylation procedure (optimal for all monosaccharides) makes the implementation of these requirements extremely difficult, which is the main reason for the relatively slow progress in the solid-phase synthesis of oligosaccharides.

Two problems seem to be especially difficult to overcome. The first of them is that successful synthesis of any biopolymer consisting of 40–50 monomeric units with a predetermined sequence (without deletions or 'erroneous' units) requires that the yield in each elongation step is no less than 97%–98%. Meanwhile, even the most advanced glycosylation methods do not ensure such high yields, which in addition vary strongly

depending on the nature of the monosaccharide and the type of the newly formed glycosidic linkage. The second problem is related to stereochemical ambiguity of the glycosylation reaction,[‡] which makes the oligosaccharide synthesis different in principle from the peptide and oligonucleotide syntheses, although it is known, for example, that the synthesis of the 1,2-*trans*-glycosidic bond is usually stereospecific. So far, the use of solid-phase synthesis is effective only for the preparation of relatively short oligosaccharides.

Yet another problem inherent in the solid-phase synthesis of oligosaccharides is related to the polyfunctionality of monosaccharides. The formation of (1-2), (1-3), *etc.*, intermonomeric glycosidic linkages requires temporary protection of hydroxy groups which are not involved in the glycosylation reaction. In the general case, synthesis of irregular oligosaccharides (*viz.*, those in which the monosaccharide components are either different or identical but differ in the type of bonding) requires specific protection depending on the type of the glycosidic bond for each monosaccharide. After the glycosylation step, the type of protection of hydroxy groups must be changed up to complete removal of the existing and introduction of new protecting groups. This sophisticated procedure makes oligosaccharide synthesis technically cumbersome in comparison with peptide and oligonucleotide syntheses. Sometimes, as in the case of homopolysaccharide synthesis, elongation of the oligosaccharide chain involves the same set of procedures, but even in these cases the passage from attachment of one monomeric fragment to the other is complicated and automation of the synthetic protocol presents a problem.

In designing a general strategy for oligosaccharide synthesis with any combination of protecting groups, it is necessary, first of all, to define the order in which the oligosaccharide chain has to be elongated. The elongation is typically carried out in two directions, *viz.*, from the reducing end of the chain to the non-reducing one (route **A**) or *vice versa* (route **B**) (Scheme 1). In the former case (route **A**), the monosaccharide immobilised on a solid support through a glycosidic hydroxyl is used as a glycosyl acceptor and

the second monosaccharide present in the solution plays the role of a glycosyl donor. In the latter case (route **B**), the first monosaccharide is attached to the support through one of the hydroxy (non-glycosidic) groups and serves as a glycosyl donor, whereas the second monosaccharide remains in the solution and fulfils the function of a glycosyl acceptor. Naturally, the protecting groups and manipulations with them in each stage of the solid-phase synthesis are different in these two routes. If the synthesis is to be performed *via* the route **A**, it is in the terminal monosaccharide of the glycosyl acceptor that the protection of the hydroxy groups should be changed or selectively removed, whereas in the case of the route **B** it is necessary to introduce or establish a group activating the glycosidic centre in the terminal monosaccharide of the glycosyl donor. Obviously, the reagents present in a solution, *e.g.*, a glycosyl acceptor (route **B**) or a glycosyl donor (route **A**), should also contain appropriate protecting groups.

Glycosylation can be carried out by chemical methods or using specific enzymes (most often, glycosyl transferases), which changes the whole strategy of the solid-phase synthesis and eliminates the problem of temporary protection of the monosaccharide units.

a. Chemical glycosylation methods

The pioneering studies of solid-phase oligosaccharide synthesis utilised classical glycosylation with glycosyl halides (predominantly, per-*O*-acetylglycosyl bromides)[§] under conditions of the Koenigs–Knorr or the Helferich reaction⁴ as well as the ortho-ester glycosylation method.²² However, insufficiently high yields and the lack of complete stereospecificity in the formation of glycosidic bonds devalue these methods for use in solid-phase synthesis. Other glycosylation methods based on the use of thio-glycosides (in the presence of activators), glycosyl tosylates,²³ glycosyl sulfoxides,²⁴ *etc.*, as glycosyl donors, have also been explored.

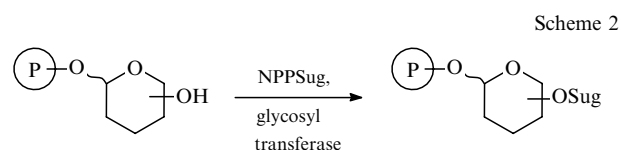
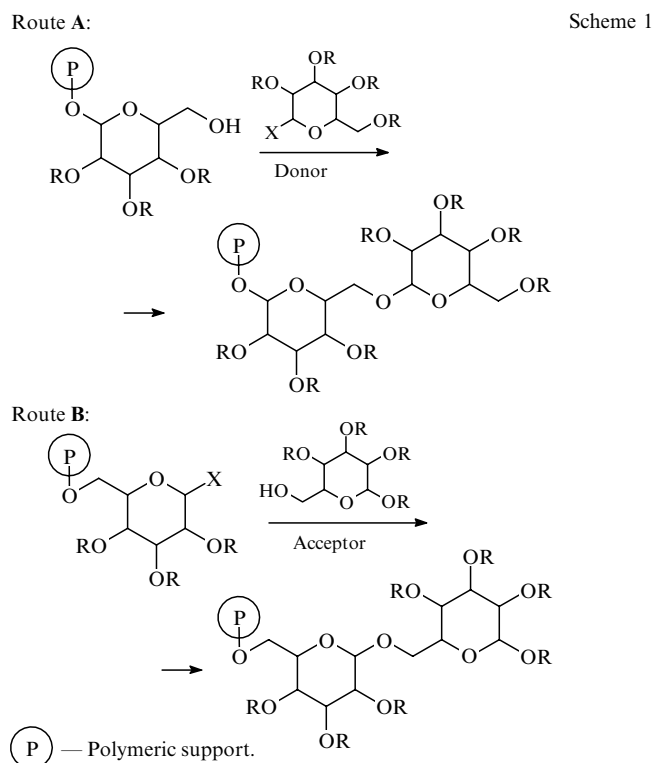
Glycosylation with sugar *O*-trichloroacetimidates proved to be especially efficient.²⁵ This procedure provides sufficiently high yields for a wide variety of monosaccharides. Unfortunately, the stereospecificity of this reaction and the effect of the configuration of the trichloroacetimidate on the steric outcome of the reaction still present a problem; therefore, the practical utility of this reaction in solid-phase synthesis of relatively high-molecular-weight oligosaccharides still remains to be elucidated.

Recently, Danishefsky *et al.*²⁶ proposed to use the so-called glycal approach²⁵ for the synthesis of relatively short oligosaccharides and glycoconjugates with more complex structures where 1,2-anhydrosugars were used as donors. This procedure has not received wide application in conventional oligosaccharide syntheses yet, but has been used to develop a convenient scheme for a solid-phase synthesis (see below).

b. Enzymic glycosylation

The elongation of the oligosaccharide chain immobilised on a support can also be carried out by biochemical methods,[¶] *i.e.*, using enzymes which transfer a monosaccharide residue from the corresponding nucleoside diphosphate sugar (NPPSug) to the end of the growing chain (Scheme 2).

The main advantages of the enzymic approach are good yields and, which is more important, high regio- and stereospecificity of



‡ A critical review of the stereospecificity of the main glycosylation reactions is given in Ref. 20.

§ An overview of various glycosylation methods is given in Ref. 21.

¶ The biosynthesis of oligosaccharides is described in a review.²⁷

glycosylation. Moreover, in this case no protection of the monosaccharide hydroxy groups is necessary, which significantly simplifies the synthetic procedure. However, sometimes the high specificity of enzymic glycosylation may have a negative effect, *viz.*, where different monosaccharides are to be introduced or different types of glycosidic bonds are to be formed. The reason is that in these cases each elongation step would require its own, specific enzyme because of the normally narrow specificities of glycosyl transferases. Moreover, the specificities of enzymes can depend both on the nature of the monosaccharide donor and the monosaccharide acceptor and on the nature of adjacent monosaccharides in the fragment of the oligosaccharide chain synthesised.

Yet another characteristic feature of enzymic glycosylation which should be taken into consideration in conducting solid-phase synthesis is a noticeable dependence of the outcome of the reaction on the nature of the support and the structure of the linker. This can be explained by the fact that the accessibility of the reaction centre of the oligosaccharide chain, which is immobilised on a solid support, for the enzyme, which itself represents a macromolecule, and the formation of an enzyme–support complex are impeded in comparison with enzymic reactions carried out in a solution. Therefore, the requirements for supports and linkers, which enable contact between the reacting molecules, are more stringent. This is the main reason why soluble and conformationally flexible polymers and structurally complex linkers are employed where enzymic methods are used for oligosaccharide synthesis on polymeric supports. (As noted above, glycosyl transferases cannot be used for enzymic oligosaccharide syntheses on polystyrene-based resins due to incompatibility of these structurally different macromolecules).

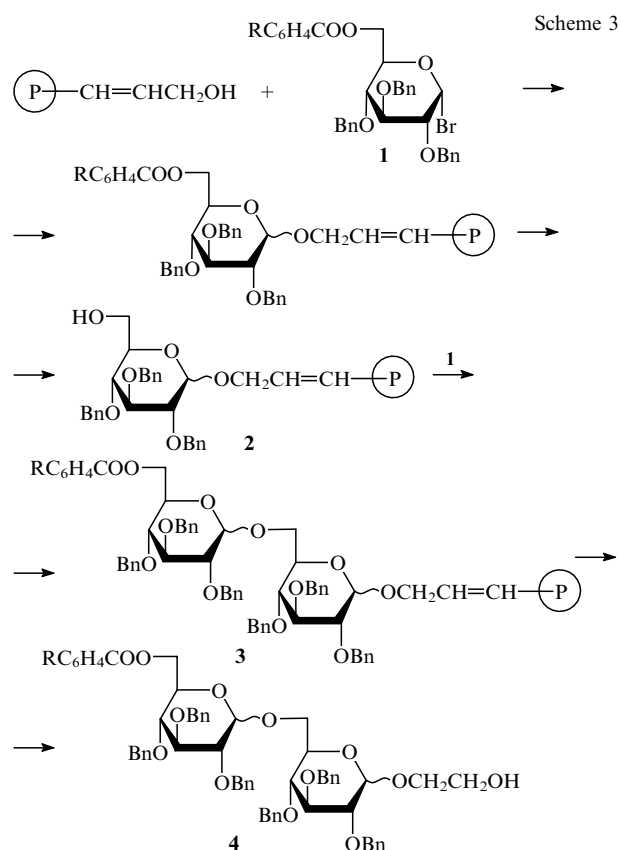
Although the first attempts to use enzymes in solid-phase syntheses of oligosaccharide date back to the 1980's, it was not until recently that this method received wide application.

III. Model syntheses of di- and trisaccharides

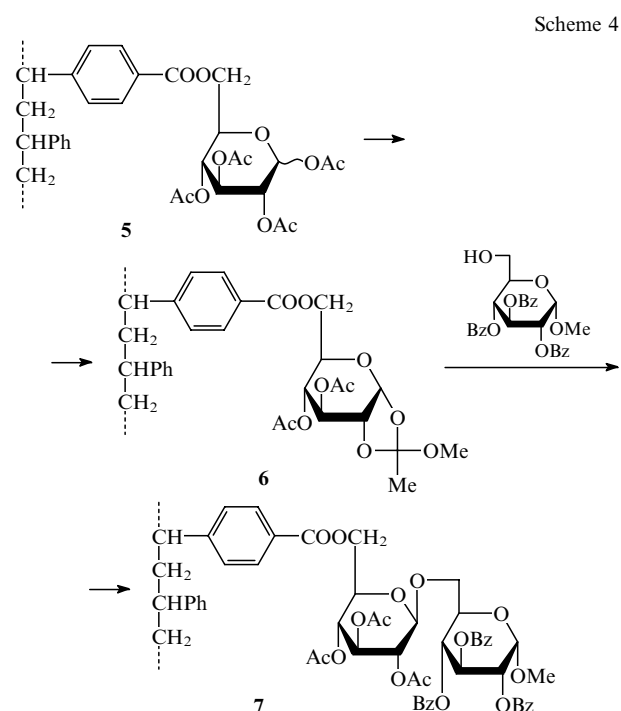
The pioneering studies on solid-phase oligosaccharide synthesis were aimed at elucidating the feasibility of this technique for preparing this class of compounds. The simplest di- and trisaccharides were the first to be synthesised.

Thus Frechet and Scheurch⁴ carried out the synthesis of D-glucopyranosyl-(1-6)-D-glucose and the corresponding trisaccharide with 1-6-bonds using elongation of the oligosaccharide chain immobilised on an insoluble support from the reducing end (Scheme 3). Treatment of a polystyrene resin modified by introduction of allyl alcohol residues²⁸ with 2,3,4-tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)-D-glucopyranosyl bromide (**1**, R = NO₂) or its *p*-methoxybenzoyl analogue (**1**, R = MeO) resulted in immobilisation of a protected glucose residue after which the acyl protection of the hydroxy group at position 6 was removed. The glucose residues in the polymer **2** were glycosylated with the same bromides. The immobilised disaccharide residues in the polymer **3** were subjected to repeated deacylation and glycosylation to obtain a trisaccharide. The polymer **3** containing disaccharide residues (or its analogue containing trisaccharide residues) was subjected to ozonolysis in order to detach the reaction product, *viz.*, the corresponding di- or trisaccharide. After reduction, the reaction products were isolated as the corresponding 2-hydroxyethyl glycosides. The disaccharide **4** represented an anomeric mixture of derivatives of α - and β -D-glucopyranosyl-(1-6)-D-glucose (*i.e.*, isomaltose and gentiobiose). Thus, the solid-phase synthesis was not stereospecific and did not differ in this respect from the corresponding reaction in solution.

An alternative scheme for the solid-phase synthesis of β -D-glucopyranosyl-(1-6)-D-glucose (gentiobiose) was proposed by Guthrie *et al.*⁵ who used an orthoester glycosylation method[†]



for the elongation of the chain (Scheme 4). The linear polymer **5**, which contained glucose residues linked through a 6-hydroxy group, was prepared by copolymerisation of styrene with 1,2,3,4-tetra-*O*-acetyl-6-*O*-(*p*-vinylbenzoyl)-D-glucopyranose or its 6-*O*-(*p*-vinylphenyl)sulfonyl analogue. The glucose residues immobilised on the polymer were converted into the corresponding 1,2-orthoester residues. The resulting polymer **6** was used as a glycosyl donor. Its reaction with methyl 2,3,4-tri-*O*-benzoyl- α -D-glucopyr-



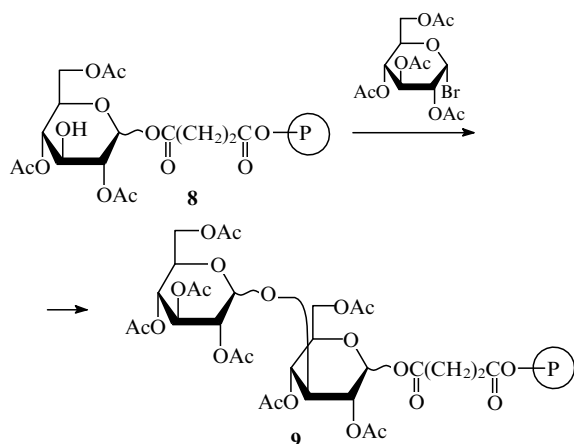
[†] For a review on the orthoester glycosylation method, see Ref. 22.

anoside under standard conditions of orthoester glycosylation afforded the gentiobiose derivative **7** (yield 64%) which was detached from the polymer by treatment with sodium methoxide. Since glycosylation of primary alcohols with orthoesters is stereospecific, this solid-phase synthesis was also stereospecific and yielded exclusively gentiobiose.

These two studies demonstrated that glycosidic bonds can be formed in heterogeneous reactions and that the value of solid-phase oligosaccharide syntheses does not exceed that of conventional syntheses in solution. Further developments in this field were aimed at overcoming some of the methodological problems, such as the choice of supports, construction of linkers suitable for support immobilisation, intermittent treatment of the polymer, *etc.* The applicability of the solid-phase approach to the synthesis of other simplest oligosaccharides was studied in parallel.

Thus the solid-phase synthesis of D-glucopyranosyl-(1-3)-D-glucose²⁹ was carried out with the aim of examining the possibility of glycosylation of a less reactive secondary hydroxy group (Scheme 5). To this end, 2,4,6-tri-*O*-acetyl-D-glucopyranose was immobilised on a polystyrene-based resin through a linker (succinic acid residue). The glycosyl acceptor **8** thus immobilised was glycosylated with 2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranosyl bromide under conditions of the Helferich reaction (48 h, 30 °C). The polymer **9** was separated and washed, after which glycosylation was repeated two more times. The acylglycosidic linkage in the polymer **9** was cleaved with hydrazinium acetate. The yield of the disaccharide, which represented a mixture of an α - (nigerose) and a β -isomer (laminaribiose) ($\sim 3:2$), was 81%.

Scheme 5



Glycosylation with 3,4,6-tri-*O*-acetyl-2-*O*-benzyl- α -D-glucopyranosyl bromide was stereospecific; the yield of the α -linked disaccharide was 55%. Thus, the feasibility of glycosylation of immobilised monosaccharides at a less reactive secondary hydroxy group under conditions of a solid-phase synthesis has been demonstrated.

In more recent studies, a succinic acid-based linker has been applied for chemical and enzymic syntheses of oligosaccharides on soluble supports. Krepinsky *et al.*³⁰ were the first to use this linker for immobilisation of the first monosaccharide on the monomethyl ether of PEG. Glycosylation of the thus immobilised monosaccharide derivatives (*e.g.*, methyl galactopyranoside, methyl 2-deoxy-2-phthalimido- β -D-glucopyranoside or 1,6-anhydro- β -D-glucopyranose) was carried out with glycosyl bromides or *O*-glycosyltrichloroacetimidates in the presence of the corresponding promoters. The resulting disaccharides[‡] were easily split off the support after completion of the synthesis. At the same time, there were some difficulties associated with the separation of the immobilised product from an excess of the glycosylating reagent

present in the solution which, as was mentioned above, is a disadvantage of the use of soluble polymers as supports.

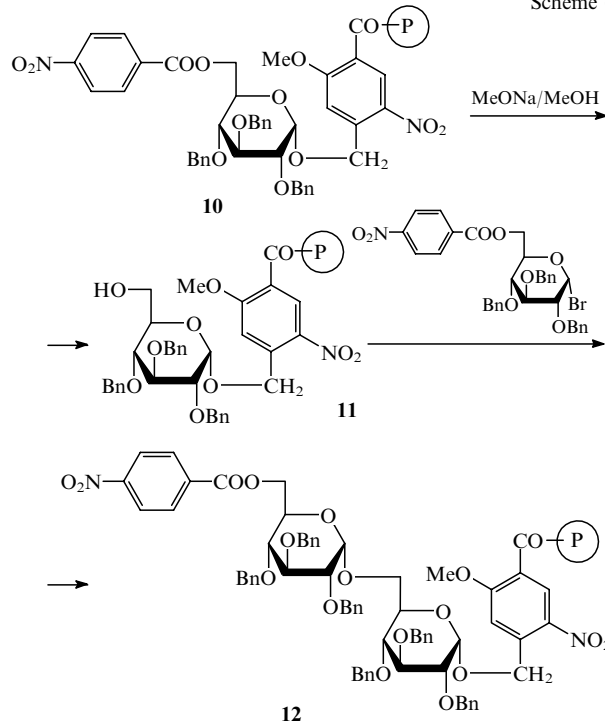
A similar approach was used in the synthesis of β -D-glucopyranosyl-(1-6)-D-galactose. In this case, the glycosyl acceptor (*viz.*, selectively protected methyl α -D-galactopyranoside with a free primary hydroxy group) was immobilised on a soluble support (Tentagel) through an OH group at position 2 or 3 using succinic acid as the linker. Glycosylation of the immobilised monosaccharide with *O*-(2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranosyl) trichloroacetimidate was stereospecific; the yield of the disaccharide liberated from the polymer by treatment with aqueous ammonia varied from 50% to 70% depending on the promoter.¹⁹

In order to facilitate detachment of oligosaccharides from the supports, it was proposed⁸ to use the thioglycoside linkage for the binding of the first monosaccharide. This linkage was formed either in a reaction of 1-thio sugars with chloromethylated polystyrene or in a reaction of acylglycosyl halides with polystyrene containing HSCH₂ groups. A model synthesis was that of gentiobiose. The resulting disaccharide was split off the polymer as benzyl glycoside by boiling in benzene containing methyl iodide and benzyl alcohol.

Zehavi *et al.*^{32–34} proposed to use 4-hydroxymethyl-3-nitrobenzoic and 4-hydroxymethyl-6-methoxy-3-nitrobenzoic acid derivatives as photosensitive linkers. The hydroxy groups of these linkers are glycosylated with monosaccharides, while the carboxy group is used for the binding to the polymeric support. The presence of an *o*-nitrobenzyl alcohol fragment enables smooth decomposition of these linkers upon photolysis in neutral media, which results in the liberation of the oligosaccharides.

These linkers were used for the first time in the synthesis of α -D-glucopyranosyl-(1-6)-D-glucose (isomaltose) (Scheme 6).³² The 2,3,4-tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)-D-glucopyranose residue was immobilised as an *O*-glycoside on a polystyrene-based resin (**10**) through the linker. The 6-OH group was deprotected by treatment with MeONa after which the polymer **11** containing partially substituted glucose residues was glycosylated with 2,3,4-tri-*O*-benzyl-6-*O*-(*p*-nitrobenzoyl)- α -D-glucopyranosyl bromide. In order to liberate the target product, which represents an isomaltose derivative, the polymer **12** was irradiated in dioxane for 32 h (yield 80%).

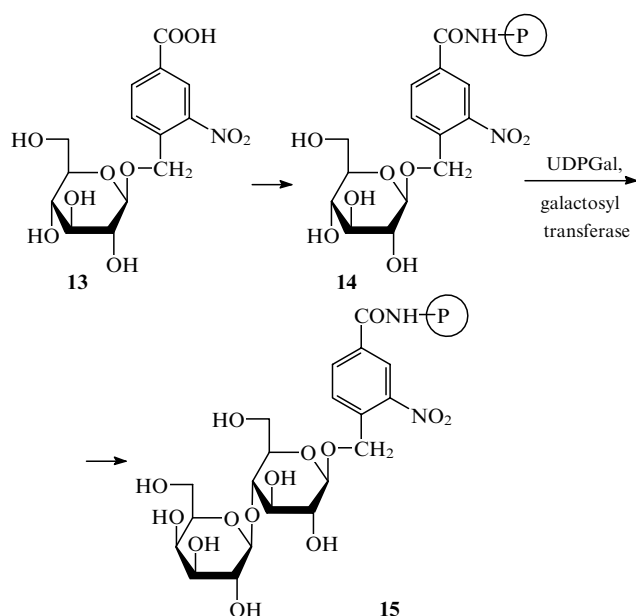
Scheme 6



[‡] For the 'methathesis' of oligosaccharides occurring in this glycosylation technique, see Ref. 31.

In more recent studies, the photosensitive linker based on 4-hydroxymethyl-3-nitrobenzoic acid was used for the enzymic synthesis of oligosaccharides on other supports. The reaction of 2,3,4,6-tetra-*O*-acetyl- α -D-glucopyranosyl bromide with alkyl 4-hydroxymethyl-3-nitrobenzoate followed by *O*-deacetylation and saponification gave the glycoside **13** (Scheme 7), which was then immobilised on modified polyacrylamide containing 2-aminoethyl groups¹³ or on modified polyvinyl alcohol bearing amino groups.³³ The glucose residues in the resulting polymers **14** were linked by glycosidic bonds and served as acceptors in enzymic syntheses. These polymers were incubated with galactosyl transferase in the presence of uridine diphosphate galactose (UDPGal) as a galactosyl donor. β -D-Galactopyranosyl-(1-4)-D-glucose (lactose) formed was split off by irradiation of the polymer **15** in aqueous solution for 20 h. This synthesis was the first to demonstrate the usefulness of glycosyl transferase in regio- and stereo-specific synthesis of a disaccharide using glycosylation of an immobilised monosaccharide residue devoid of protecting groups.

Scheme 7



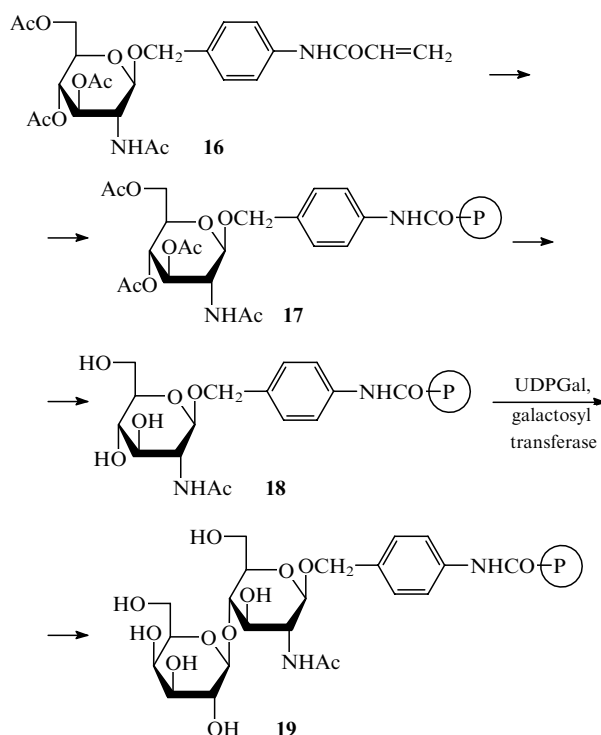
Similarly, the glycosylation of 4-hydroxymethyl-3-nitrobenzoic acid immobilised on polyacrylamide with cellobiose 1,2-orthoester and subsequent deacetylation afforded a polymer containing cellobiose residues with free hydroxy groups. These played the role of acceptors in the enzymic reaction with galactosyl transferase and UDPGal which gave the trisaccharide β -Galp(1-4)- β -Glc(1-4)Glc. Cellobiose immobilised on polyacrylamide was also used in the synthesis of oligosaccharides containing *N*-acetyl- β -D-glucosamine residues which were transferred from chitin in the presence of lysozyme.¹³

Maltose [α -Glc(1-4)Glc], maltotriose [α -Glc(1-4)- α -Glc(1-4)Glc] and panose [α -Glc(1-6)- α -Glc(1-4)Glc] were immobilised on *N*-(2-aminoethyl)polyacrylamide through the same photosensitive linker in order to investigate the specificity of glycogen synthase, which transfers glucose residues from uridine diphosphate glucose (UDPG) to glucooligosaccharides, and to elucidate the role of primers in the biosynthesis of glycogen.³⁴ Oligosaccharide derivatives were attached to 4-hydroxymethyl-3-nitrobenzoic acid; the resulting glycosides were deacylated and immobilised on a polymer through the carboxy group of the linker by treatment with water-soluble carbodiimide. Reactions of these immobilised acceptors with UDPG in the presence of glycogen synthase shed additional light on some essential details of the mechanism of glycogen biosynthesis, *e.g.*, the role of primers, the appearance of branching, *etc.*

In the enzymic synthesis of *N*-acetylglucosamine [2-acetamido-4-*O*-(β -D-galactopyranosyl)-2-deoxy-D-glucose],³⁵ the *N*-acetylglucosamine residue was immobilised on a water-soluble copolymer of acrylamide and *N*-acryloyloxysuccinimide modified by incorporation of 2-aminoethyl groups through its glycosidic centre and a photosensitive linker (*viz.*, 4-hydroxymethyl-3-nitrobenzoic acid). After *O*-deacetylation of the glucosamine residue, the polymer was incubated with UDPG in the presence of the UDPG epimerase–galactosyl transferase system which provided epimerisation of the glucose residue and transfer of the galactose residue to the acceptor. The *N*-acetylglucosamine thus formed was liberated from the polymer by photolysis.

Copolymerisation of acrylamide with its derivative **16** (Scheme 8) gave rise to polyacrylamide **17** bearing glucosamine residues glycosidically linked to a benzyl-type linker. After *O*-deacetylation, the polymer **18** was incubated with UDPGal and galactosyl transferase. The resulting *N*-acetylglucosamine **19** was split off the polymeric carrier by hydrogenolysis in the presence of Pd/C.³⁶

Scheme 8



These examples illustrate that the use of enzymes in solid-phase synthesis of oligosaccharides is promising. The efficacy of enzymic elongation of oligosaccharide chains depends on the distance between the monosaccharide acceptor and the surface of the support. This distance and, as a consequence, the optimum size of the linker, are determined by the molecular mass of the enzyme. If the galactose residue is transferred by galactosyl transferase, it can be attached to the polymer by a chain containing only two methylene units, whereas successful glucose transfer effected by glycogen synthase with a higher molecular mass requires that the chain contained at least six methylene units.

The solid-phase syntheses of di- and trisaccharides described above do not have any obvious advantages over the corresponding syntheses in solution. However, they provided a clue to the solution of some urgent methodological problems in order to pass to targeted synthesis of fragments of homo- and heteropolysaccharides and glycopeptides and contributed also to progress in the combinatorial chemistry of carbohydrates.

IV. Synthesis of higher oligosaccharides

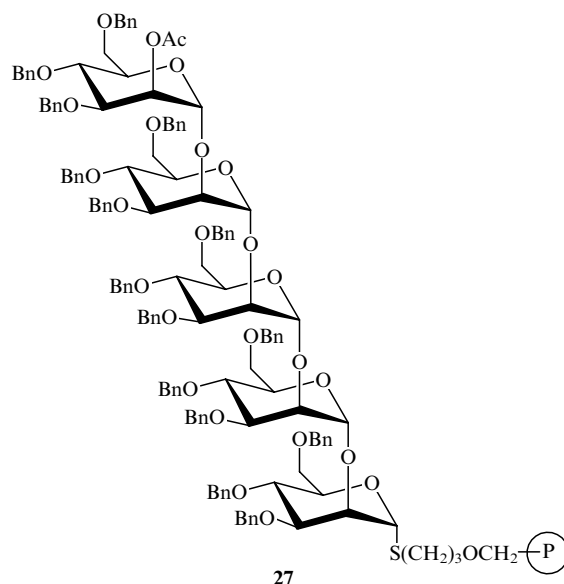
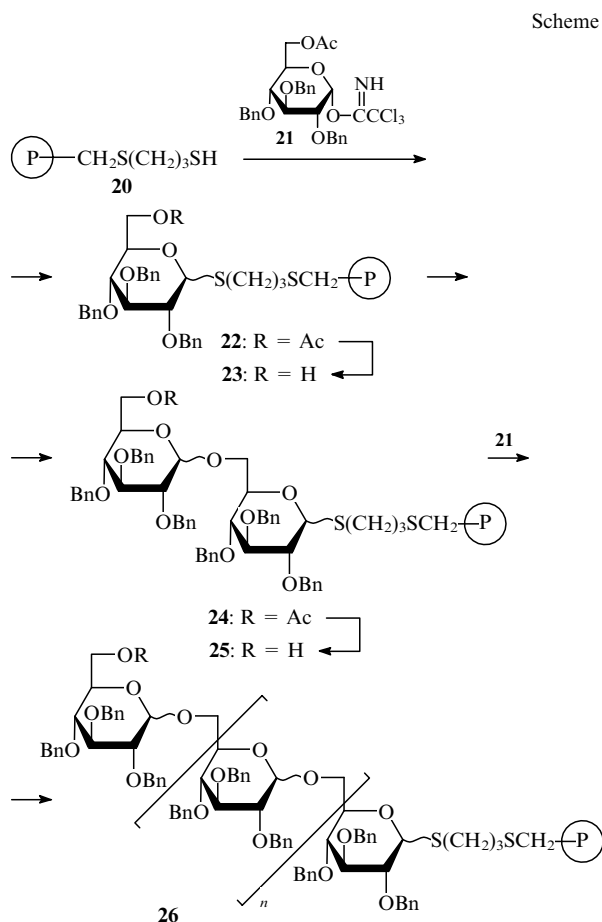
Several solid-phase syntheses of regular homooligosaccharides containing up to 10 monosaccharide units have been carried out to date. Although some of compounds of this type can be prepared by polymerisation of monosaccharide derivatives,^{37,38} their synthesis on solid supports made it possible to develop a standard procedure for stepwise elongation of an oligosaccharide chain suitable for concrete method of glycosylation.

Gluco- and manno oligosaccharides were prepared by the Schmidt trichloroacetimidate method,³⁹ which is the most popular. The synthesis of (1-6)-D-gluco oligosaccharides is shown in Scheme 9. The polymer **20** modified with 3-mercaptopropylthiomethyl groups was prepared by the reaction of the Merrifield polymer with propane-1,3-dithiol. The substituted glucose residue was attached to the free thiol group of the polymer to form the thioglycosidic bond using *O*-(6-*O*-acetyl-2,3,4-tri-*O*-benzyl-D-glucopyranosyl) trichloroacetimidate (**21**). The 6-*O*-acetyl group in the resulting polymer **22** was removed and the polymer **23** formed was treated with a threefold excess of the imidate **21** in the presence of trimethylsilyl triflate. The *O*-acetyl group in the polymer **24** was removed again, the polymer **25** was glycosylated by treatment with the glycosyl donor **21**, and the whole procedure was repeated as many times as required. After termination of the synthesis, the oligosaccharide was split off from the polymer **26** with a thiophilic reagent [e.g., dimethyl(methylthio)sulfonium triflate] in the presence of a base. This approach was used in the synthesis of di-, tri-, tetra- and pentasaccharides. The yields of the products in each step of the chain elongation were determined by the increase in the polymer mass. In addition, this reaction was monitored by a mass-spectrometric procedure which had been specially developed for this purpose. An aliquot of the polymer was treated with dimethyl(methylthio)sulfonium tetrafluoroborate in a dichloromethane–methanol mixture in the presence of

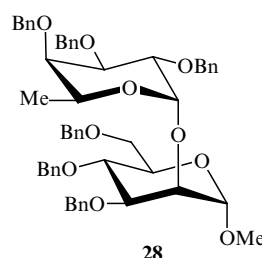
the Hünig base and the oligosaccharides liberated were analysed by mass spectrometry, which made it possible to judge the completeness of glycosylation in each step. According to mass spectrometric data (MALDI–TOF), the yield was 95%.

Each glycosylation step afforded a mixture of α - and β -anomers in an α : β ratio of 1:1; thus, the pentamer represented a mixture of 32 diastereomers. Hence, this methodology is well-suited for combinatorial syntheses.

A similar approach was used in the synthesis of α -1,2-linked oligomannosides.¹¹ 2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-D-mannopyranose residues were incorporated into the polystyrene resin $(\text{P})\text{-CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{SH}$ prepared in an analogous way. After deacetylation and glycosylation of the deacetylated product with *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-D-mannopyranosyl) trichloroacetimidate and reiteration of the reaction cycle, the immobilised oligomannosides **27** (up to the hexasaccharide) were split off the support by treatment with *N*-bromosuccinimide in THF–MeOH in the presence of 2,6-di-*tert*-butylpyridine. The elongation of the chain was monitored by mass spectrometry. The yields of di-, tri- and tetramannosides were 75%, 54% and 34%, respectively.

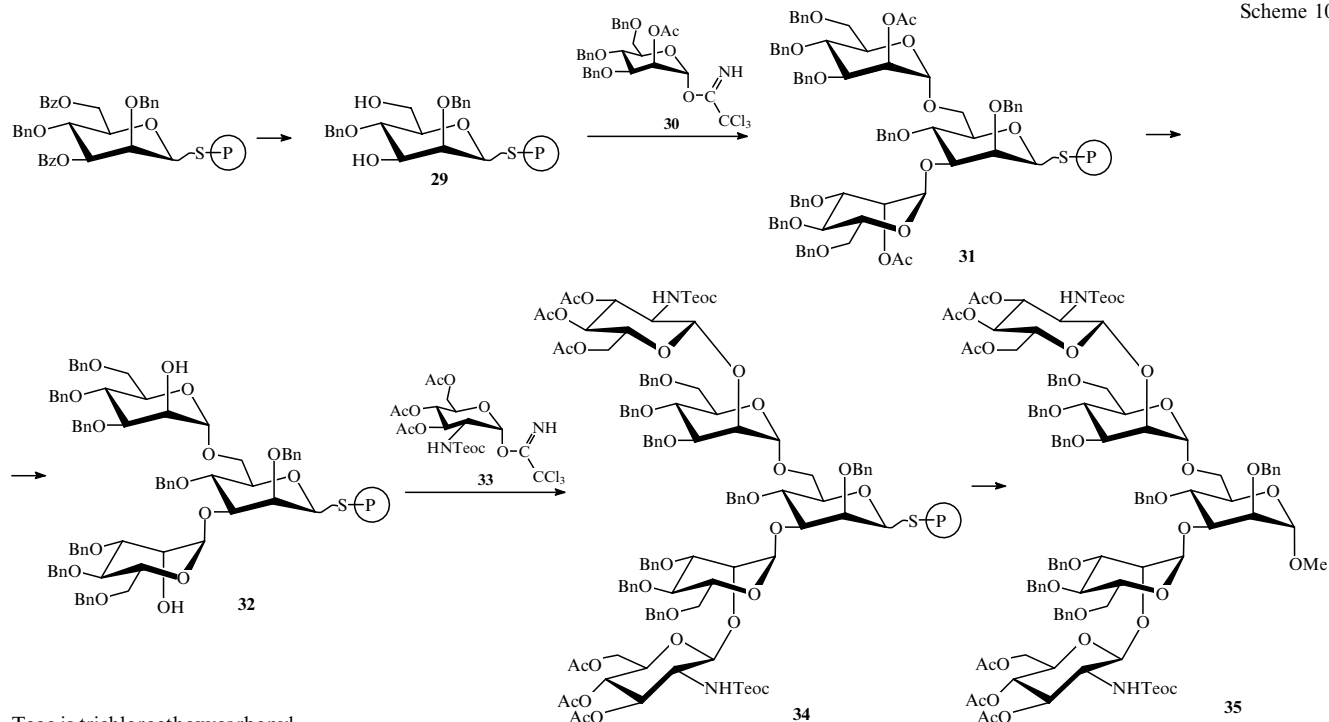


Glycosylation of the first mannose residue with an L-fucose analogue instead of *O*-mannosyl trichloroacetimidate yields the disaccharide **28** containing an α -L-fucosidic (1,2-*cis*-glycosidic) bond.



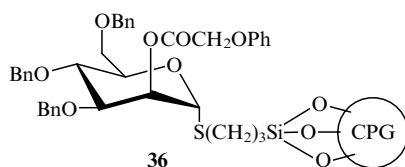
This approach was also used in the synthesis of a well-known core of *N*-glycoproteins, which represents a branched pentasaccharide (Scheme 10).¹² Mannose residues were immobilised on the same polymer, viz., $(\text{P})\text{-CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{SH}$, by treatment with *O*-(2,4-di-*O*-benzyl-3,6-di-*O*-benzoyl- α -D-mannopyranosyl) trichloroacetimidate. Both benzoyl groups in the resulting polymer were removed, and the diol **29** formed was glycosylated with an excess of *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl- α -D-mannopyranosyl) trichloroacetimidate (**30**). The acyl groups in the polymer **31** were removed again, and the immobilised trisaccharide **32** was glycosylated with *O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-trichloroethoxycarbonylamino- α -D-glucopyranosyl) trichloroacetimidate

Scheme 10



(33), which afforded a polymer with an immobilised pentasaccharide (34). The thioglycosidic linkage was cleaved with *N*-bromosuccinimide in the presence of methanol and 2,6-di-*tert*-butylpyridine resulting in the pentasaccharide 35 in 20% yield; hence, the yield of glycosylation was 85% in each step. The yields of the reaction products were monitored by mass spectrometry, while the stereochemistry of the glycosidic bonds was established by NMR spectroscopy.

Analogous syntheses of α -(1-2)-linked manno oligosaccharides were performed on other supports as well, *e.g.*, on porous glasses with grafted mercaptopropyl groups.⁴⁰ The 3,4,6-tri-*O*-benzyl-2-*O*-phenoxyacetyl-D-mannose residues were attached to the support modified by treatment with 3-mercaptopropyltrimethoxysilane. The phenoxyacetyl group in the immobilised saccharide 36 was removed with guanidine and the next mannose residue was attached to the liberated hydroxy group after which the whole reaction cycle was reiterated. The oligomannoside synthesised was split off the support by treatment with *N*-bromosuccinimide in the presence of methanol and 2,6-di-*tert*-butylpyridine. Mass-spectrometric analysis revealed that the resulting trisaccharide contained only trace amounts of the mono- and the disaccharide, which suggests that glycosylation occurred with high yields in each step.



Synthesis of this type of oligomannosides have also been carried out on a soluble support, *viz.*, monomethyl ether of polyethyleneglycol.¹⁷ 1,4-Bis(hydroxymethyl)benzene⁸ has been used as a linker and 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-D-mannopyr-

anose residue was attached through this linker. The elongation of the oligosaccharide chain was carried out as described above. A scandium(III) triflate-acetic anhydride system was recommended for the splitting of the reaction product from the polymer.⁴¹

In all these oligomannoside syntheses, the chain was elongated from the reducing end to the non-reducing one. However, an alternative route is documented, which utilises an opposite strategy, *i.e.*, the elongation is performed from the non-reducing end of the chain to its reducing end. The synthesis on the soluble support (PEG) was carried out according to the following scheme.⁴² The linker used was a 6-(4-hydroxymethylphenoxy)-hexanoic acid derivative, which alkylated methyl 3,4,6-tri-*O*-benzyl-1-thio- α -D-mannopyranoside at position 2 and esterified PEG (Scheme 11). The substituted methyl 1-thiomannopyranoside residue in the polymer 37 served as the glycosyl donor, reacted with 3,4,6-tri-*O*-benzyl-D-mannopyranosyl fluoride in the presence of methyl triflate to give the disaccharide derivative 38 which also played the role of a glycosyl donor. The Suzuki glycosylation⁴³ of 2-(trimethylsilyl)ethyl 3,4,6-tri-*O*-benzyl- α -D-mannopyranoside resulted in the immobilised trisaccharide 39; the free trisaccharide was split off the polymer by treatment with a base and deprotected by hydrogenolysis.

The target product (yield 40%) was easily separated from by-products owing to the presence of a hydrophobic trimethylsilyl-ethyl group.

Incorporation of hydrophobic groups to facilitate isolation of the target product was also used⁴² in the synthesis of a structurally more complex heterooligosaccharide 40, which is a fragment of glycosphosphatidylinositol. The latter was prepared by a reaction of the disaccharide 41 with the glycosyl donor 38. The tetrasaccharide 40, which was cleaved from the polymer 40p by hydrogenolysis, could easily be purified by reversed-phase chromatography owing to the presence of hydrophobic phthalimido- and methoxyphenyl groups. This methodology is an interesting example of modification of carbohydrate synthesis on solid phase supports.

From the oligomannoside syntheses described above one cannot draw any final conclusion in favour of one or another synthetic procedure, but the flexibility and high potential of the solid-phase method have been demonstrated.

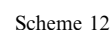
§ It should be noted that this type of linker has also been used in some other syntheses on soluble supports, *e.g.*, in the synthesis of model disaccharides.


$$\beta\text{-Gal}f(1\text{-}5)[\beta\text{-Gal}f(1\text{-}5)]_5\beta\text{-Gal}f\text{OCH}_2\text{CH}_2\underset{\text{NH}_2}{\underset{|}{\text{CH}}}\text{COOH}$$

42

Further developments in solid-phase oligosaccharide synthesis were aimed at a search for novel methods of glycosylation. The

so-called glycal method (Scheme 13) ¹⁰ offers the most interesting opportunities for the synthesis of complex (including branched) oligosaccharides. After treatment with a mild epoxidising reagent (*viz.*, 3,3-dimethyldioxirane), the glycal **48** immobilised on a support through a hydroxy group is converted into the 1,2-anhydrosugar **49**. The latter reacted with the glycal **50** with a free



Tr = Ph₃C; Z = PhCH₂OCO; Piv = Me₃CCO; Lev = MeCO(CH₂)₂CO.

The reaction scheme illustrates the synthesis of phosphonate-protected nucleosides. It begins with nucleoside **48**, which has a phosphate group at the 5' position and a double bond between the 2' and 3' carbons of the sugar ring. Oxidation ([O]) of **48** yields intermediate **49**, where the double bond has been converted to an epoxide ring. Intermediate **49** then reacts with nucleoside **50** (a nucleoside with a 2,6-dimethyl-4-hydroxyphenyl group at the 1' position) to form intermediate **51**. Intermediate **51** is a dimeric structure where the 3' carbon of the sugar in **49** is linked via an oxygen atom to the 5' carbon of the sugar in **50**. Finally, oxidation ([O]) of **51** yields intermediate **52**, where the double bond in the sugar of **50** has been converted to an epoxide ring. Intermediate **52** then reacts with nucleoside **53** (a nucleoside with a 2,6-dimethyl-4-hydroxyphenyl group at the 1' position and a hydroxyl group at the 3' position) to form the final product **54**. Intermediate **54** is a dimeric structure where the 3' carbon of the sugar in **52** is linked via an oxygen atom to the 5' carbon of the sugar in **53**.

Scheme 1

55 + 56 $\rightarrow$ 58 $\xrightarrow{57}$ 59 $\xrightarrow{56}$ 60 $\xrightarrow{57}$ 61 $\xrightarrow{50a}$ 62 $\xrightarrow{57}$ 63 $\xrightarrow{65}$ 64 $\xrightarrow{57}$ 65 $\xrightarrow{50a}$ 66 $\xrightarrow{65}$ 67

R = Ph, Prⁱ.

$$R = \text{Ph, Pr}^i.$$

hydroxy group in the presence of ZnCl_2 to yield the disaccharide glycal **51** which is further converted into the 1,2-anhydrosugar **52**. Its reaction with the monosaccharide glycal **53** afforded the immobilised trisaccharide glycal **54**, and so on. The yields in each glycosylation step amounted to 90%–95%. High stereospecificity of glycosidic linkage formation is governed by well-established regularities in the epoxide ring opening. As can be seen, the main characteristic feature of this approach is the reconstruction of a reactive epoxide group (*i.e.*, a glycosyl donor group) at the reducing end of the growing chain under standard mild conditions. By varying the structure of the glycal acceptor, one can obtain both regular and irregular homo- and heterooligosaccharides. Immobilised glycals with free hydroxy groups resulting either from the reaction or after selective removal of protecting groups can also play the role of glycosyl acceptors which permits their glycosylation leading to branched oligosaccharides.

It should be emphasised that the use of the glycal method simplifies the purification of the reaction product, since possible admixtures formed as a result of incomplete glycosylation in the intermediate steps of the synthesis become more polar after final treatment and can easily be separated from the target oligosaccharides by chromatography.

The high potentials and flexibility of the glycal method can be exemplified in the convergent synthesis of several oligosaccharides on an insoluble support (Scheme 14).¹⁰ Here, R_2SiCl groups ($\text{R} = \text{Ph}$, Pr^i), which are used as linkers for binding the first monomer to the polymeric support, were incorporated into a polystyrene resin by sequential treatment with butyllithium and diphenyl- or diisopropyldichlorosilane. The use of such linkers allows easy cleavage of the $\text{O}-\text{Si}$ bond upon treatment with Bu_4NF , which enables detachment of the synthesised product from the support under mild conditions.

Treatment of the thus modified polystyrene **55** with a D-galactal derivative **56** in the presence of a base followed by oxidation with dimethyldioxirane (**57**) affords the polymer **58**, which contains the immobilised anhydrosugar residue, which is employed as the glycosyl donor for the elongation of the chain. Glycosylation of the polymer **58** with D-galactal **56** in the presence of anhydrous ZnCl_2 yields the disaccharide glycal derivative **59**. Reiteration of the reaction cycle results in the trisaccharide glycal **60**; its reaction with 3,4-di-*O*-benzyl-D-glucal (**50a**) yields the tetrasaccharide glycal **61** with (1-6) glycosidic linkages. The introduction of a structurally different glycal acceptor (*e.g.*, 4,6-*O*-benzylidene-D-glucal **62**) into the reaction with an immobilised glycosyl donor prepared from the trisaccharide glycal **60** results in the formation of the tetrasaccharide glycal **63** of irregular structure. After

conversion into the glycosyl donor, the glycal **63** reacts with 3,4-di-*O*-benzyl-D-glucal as described above to yield the irregular pentasaccharide derivative **64**. Finally, oxidation of the trisaccharide glycal **60** and subsequent reaction with the disaccharide glycal **65** afforded the pentasaccharide glycal **66**. Conversion of the tetrasaccharide glycal **63** into a glycosyl donor using the conventional scheme and reaction of the latter with the disaccharide glycal **65** result in the hexasaccharide derivative **67**.

In each step of this convergent synthesis, the oligosaccharides can be split off the polymer by treatment with Bu_4NF and protecting groups can be removed by standard methods. The yields of the oligosaccharides are 80%–90% in each step, which gives the final yields of the order of 20% to 40%. The stereochemistry of glycosidic linkages in all steps of this synthesis was established by NMR spectroscopy.

The usefulness of two other, recently proposed glycosylation methods for solid-phase synthesis, *viz.*, those utilising glycosyl sulfoxides²⁴ and pent-4-enyl glycosides⁴⁵ as glycosyl donors, is more difficult to evaluate.

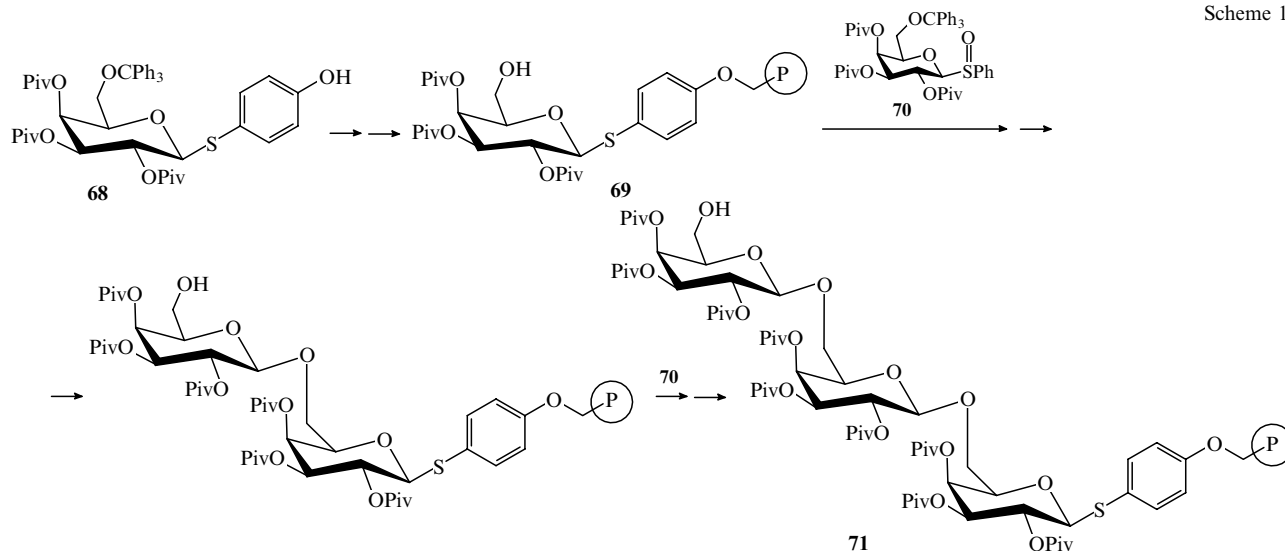
Several examples of solid-phase syntheses with the use of these glycosylating reagents are considered below.

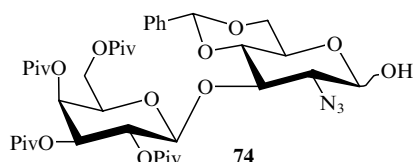
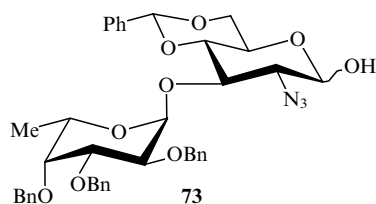
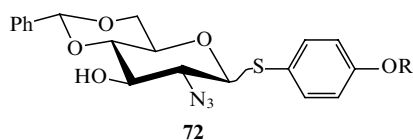
p-Hydroxyphenyl 2,3,4-tri-*O*-pivaloyl-6-*O*-trityl-1-thio- β -D-galactopyranoside (**68**) was immobilised on Merrifield's resin (Scheme 15).²⁴ After removal of the trityl group from the immobilised monosaccharide, the hydroxy group in the polymer **69** was glycosylated with the sulfoxide **70** in the presence of trifluoromethanesulfonic acid anhydride and 2,4,6-tri-*tert*-butylpyridine. After removal of the trityl group from the immobilised disaccharide, the reaction sequence was repeated. The resulting derivative of the corresponding trisaccharide **71** was split off the support by treatment with mercury trifluoroacetate in a dichloromethane–water mixture. The glycosylation occurred stereospecifically with formation of a β -galactosidic bond. The yield of the trisaccharide was 52%. Taking into account the fact that only 70% to 75% of the oligosaccharide is liberated from the polymer, the yields of di- and trisaccharides in the glycosylation step were no less than 94%–95%.

Glycosyl sulfoxides can be used as glycosyl donors in the glycosylation of secondary hydroxy groups as is exemplified in the synthesis of two synthetic precursors of Lewis antigens of group-specific blood glycoproteins.

Glycosylation of 2-azido-4,6-*O*-benzylidene-2-deoxy-1-thio-D-glucoside immobilised in an analogous way (**72**) with sulfoxides based on 2,3,4-tri-*O*-benzyl-L-fucose and 2,3,4,6-tetra-*O*-pivaloyl-D-galactose afforded the disaccharides **73** and **74** (yields 67% and 64%, respectively); these reactions were stereospecific.

Scheme 15





The stereospecificity of these reactions, which is particularly emphasised by the authors,²⁴ is quite obviously governed by the nature of a substituent at the O(2) of the glycosyl donor. The same regularity is observed when glycosylation is carried out in solution.

Further utilisation of glycosyl sulfoxides in solid-phase syntheses of oligosaccharides is still not documented.

Rather specific experimental conditions and uncertainty of the problem of stereospecificity in the case of other monosaccharides seem to preclude the widespread application of glycosylation based on the use of glycosyl sulfoxides.

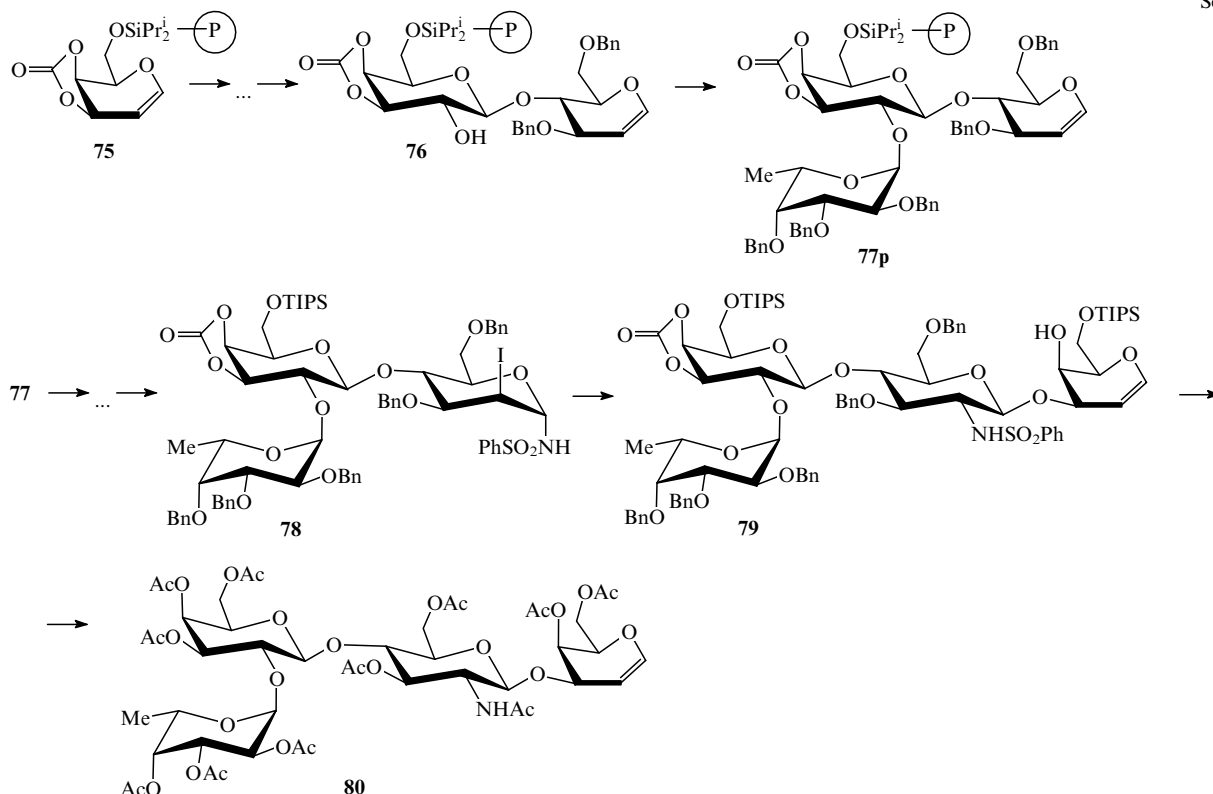
Pent-4-enyl glycosides act as glycosylating agents following generation of a carbocation at the glycosidic centre of the sugar as a result of treatment with *N*-iodosuccinimide and triethylsilyl triflate. The glycosylation with *n*-pent-4-enyl glycosides has been described in detail;⁴⁵ some general considerations concerning the applicability of this reaction to solid-phase syntheses on different

supports, with different linkers and monosaccharides were briefly surveyed in Ref. 46. According to Fraser-Reid *et al.*,⁴⁶ solid-phase glycosylation gives satisfactory yields. Since the stereoselectivity of this reaction is not very high, it is recommended for use in combinatorial chemistry for the acquisition of 'libraries' of immobilised oligosaccharides designed for direct activity assays. The principles common to combinatorial chemistry have been applied for the acquisition of a library of deprotected oligosaccharides concomitant with the synthesis of the trisaccharide β -Galp(1-2)- α -Glc(1-6)GlcNAc (no experimental details were given).

The advantages of solid-phase oligosaccharide synthesis are most conspicuous in the directed synthesis of complex fragments of natural biopolymers. Thus, the glycal method was used in the synthesis of a series of biologically important oligosaccharides which play an essential role in carbohydrate-protein interactions and represent antigenic determinants. Some steps of this synthesis were carried out on a polystyrene support.

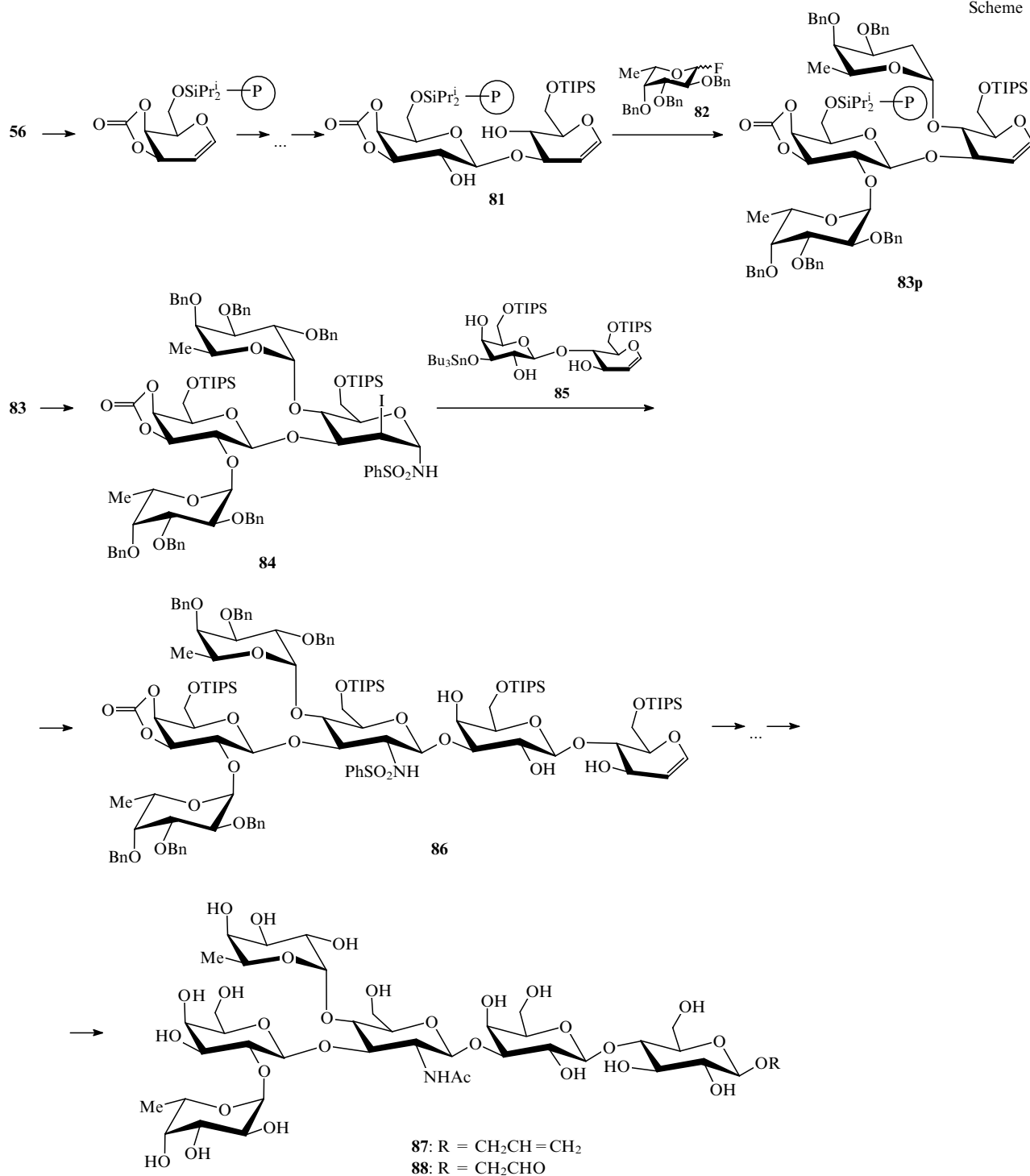
The synthesis of the blood-group H-determinant (type 2) is shown in Scheme 16.⁴⁷ 3,4-*O*-Carbonyl-D-galactal **75** immobilised on a polystyrene resin through a diisopropylsilyl linker was oxidised with dimethyldioxirane into the corresponding 1,2-anhydrosugar which was then introduced into a reaction with 3,6-di-*O*-benzyl-D-glucal in the presence of ZnCl_2 . The resulting immobilised disaccharide glycal **76** was glycosylated at the free OH group at position 2' with 2,3,4-tri-*O*-benzyl-L-fucopyranosyl fluoride in the presence of tin triflate and 2,6-di-*tert*-butylpyridine. The immobilised trisaccharide **77p** was treated with Bu_4NF to liberate the trisaccharide **77** (overall yield was 50%) after which the synthesis was continued in the solution. The hydroxy group at C(6) of the galactose residue in the trisaccharide **77** was protected with a triisopropylsilyl group and treated with benzenesulfamide in the presence of iodonium(dicollidine) perchlorate. The resulting 2-deoxy-2-iodo-*N*-phenylsulfonylglycosylamine **78** (*cf.* Ref. 48) underwent rearrangement in a reaction with 3-*O*-tributylstannyl-6-*O*-triisopropylsilyl-D-galactal in the presence of silver tetrafluoroborate.⁴⁹ The resulting tetrasaccharide **79** was subjected to

Scheme 16



TIPS = SiPr_3 .

Scheme 17



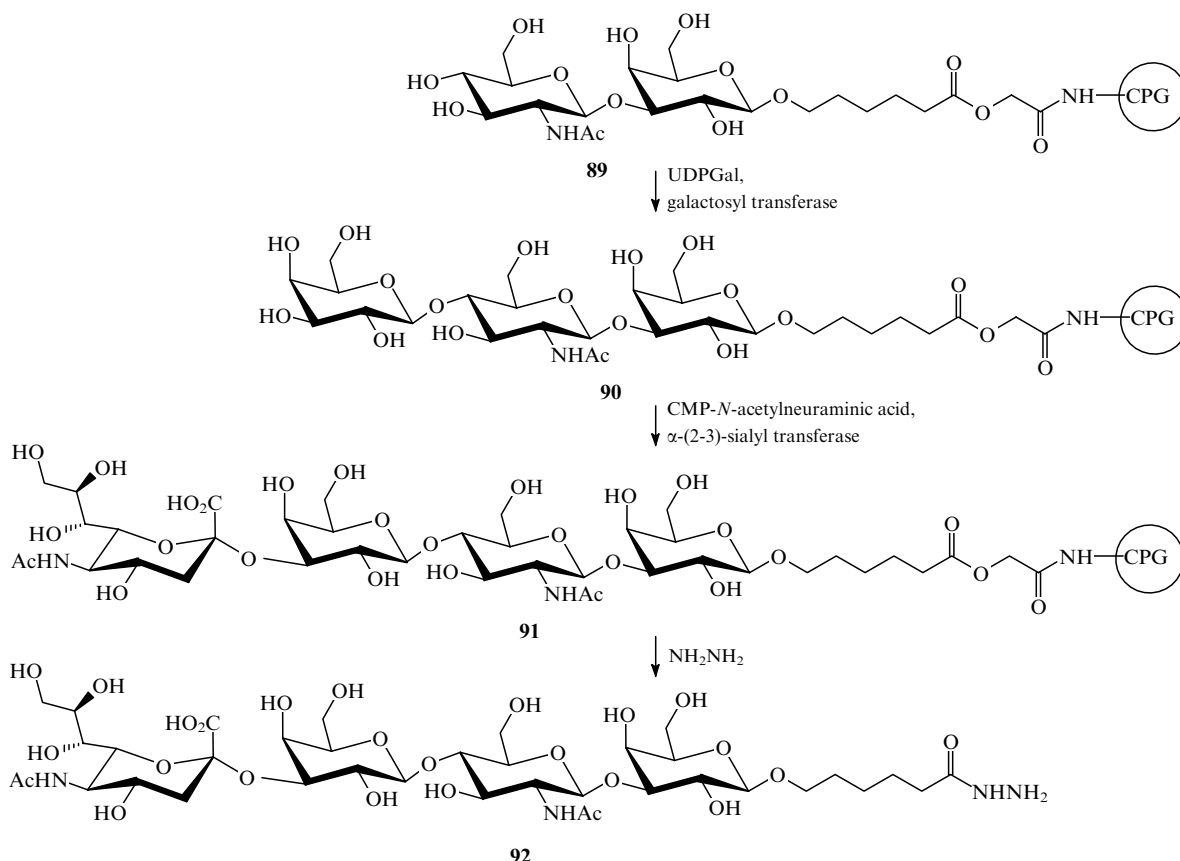
deprotection and *N*-acetylation to give the tetrasaccharide **80**, which is a derivative of the H-antigen (type 2) of a blood group-specific glycoprotein.

A similar approach was used in the synthesis of a Le^b -specific hexasaccharide, which was prepared in a form suitable for conjugation with proteins (Scheme 17).⁴⁷ The starting galactal **56** was immobilised on a polystyrene resin; the reaction product was converted into an 1,2-anhydrosugar, which further glycosylated 6-*O*-triisopropylsilyl-D-glucal [its most reactive hydroxy group at C(3) reacts selectively]. The (1-3)-linked disaccharide **81** with two free hydroxy groups was glycosylated with an excess of 2,3,4-tri-*O*-benzyl-L-fucopyranosyl fluoride (**82**). The resulting tetrasaccharide **83p** bearing two L-fucose residues was split off the support, the primary alcohol groups in the tetrasaccharide liber-

ated were silylated after which the synthesis was continued in solution. The tetrasaccharide **83** was converted into tetrasaccharide 2-deoxy-2-iodo-*N*-phenylsulfonylglycosylamine **84**. The latter reacted with 3-*O*-tributylstannyl-L-fucose derivative **85** to give the hexasaccharide glycal **86**, which was converted into an 1,2-anhydro derivative and then made to react with allyl alcohol to obtain the allyl glycoside of the corresponding hexasaccharide **87**. To prepare antibodies against Le^b antigen, the hexasaccharide **87** was converted into the aldehyde **88** suitable for conjugation with proteins.

Halcomb *et al.*¹⁵ performed an enzymic synthesis in solution of the pentasaccharide NeuAc- α -(2-3)-Gal- β -(1-4)-[Fuc- α -(1-3)]-GlcNAc- β -(1-3)-Gal and an enzymic solid-phase synthesis of the tetrasaccharide NeuAc- α -(2-3)-Gal- β -(1-4)-GlcNAc- β -(1-3)-Gal,

Scheme 18



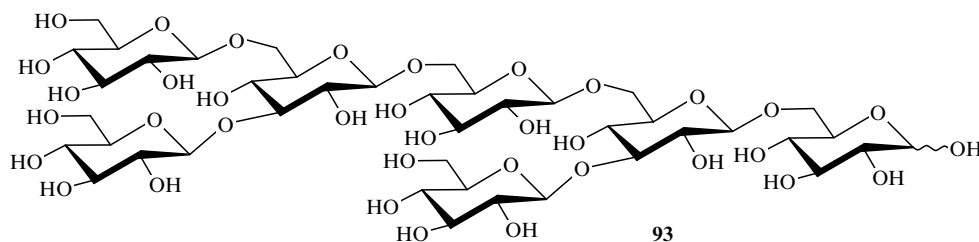
which are known as inhibitors of E-selectin and *Helicobacter pylori*, respectively. A fragment of the pentasaccharide, viz., the tetrasaccharide NeuAc- α -(2-3)-Gal- β -(1-4)-[Fuc- α -(1-3)]-GlcNAc (sialyl-Lewis X, SLe^X), is a tumour-associated antigen; it is involved in processes of cell adhesion, metastasis, inflammation and thrombosis. This antigen contains neuraminic acid; its stereospecific introduction into oligosaccharides by chemical methods presents a problem, therefore the use of enzymic glycosylation is more preferable in this case.

The solid-phase synthesis of the tetrasaccharide NeuAc- α -(2-3)-Gal- β -(1-4)-GlcNAc- β -(1-3)-Gal was performed on CPG modified with iodoacetyl amino groups, which made it possible to conduct the synthetic operations in both aqueous solution and organic solvents as required (Scheme 18).¹⁵ The starting disaccharide, viz., 2-acetamido-2-deoxy- β -D-glucopyranosyl-(1-3)-D-galactopyranose, prepared by chemical synthesis as a glycoside of ω -hydroxyhexanoic acid, was immobilised on the modified CPG. After incubation with UDPGal in the presence of β -(1-4)-galactosyl transferase, the immobilised disaccharide **89** yielded the trisaccharide **90**, which was made to react with cytidine 5'-phospho-*N*-acetylneuraminic acid (CMP-*N*-acetylneuraminic acid) in the presence of α -(2-3)-sialyl transferase. The resulting tetrasaccharide **91** was split off the support with hydrazine and isolated as ω -hydroxyhexanohydrazide glycoside **92** suitable for conjugation with proteins. This synthesis demonstrates again the advantages of the enzymic approach in solid-phase oligosaccharide syntheses

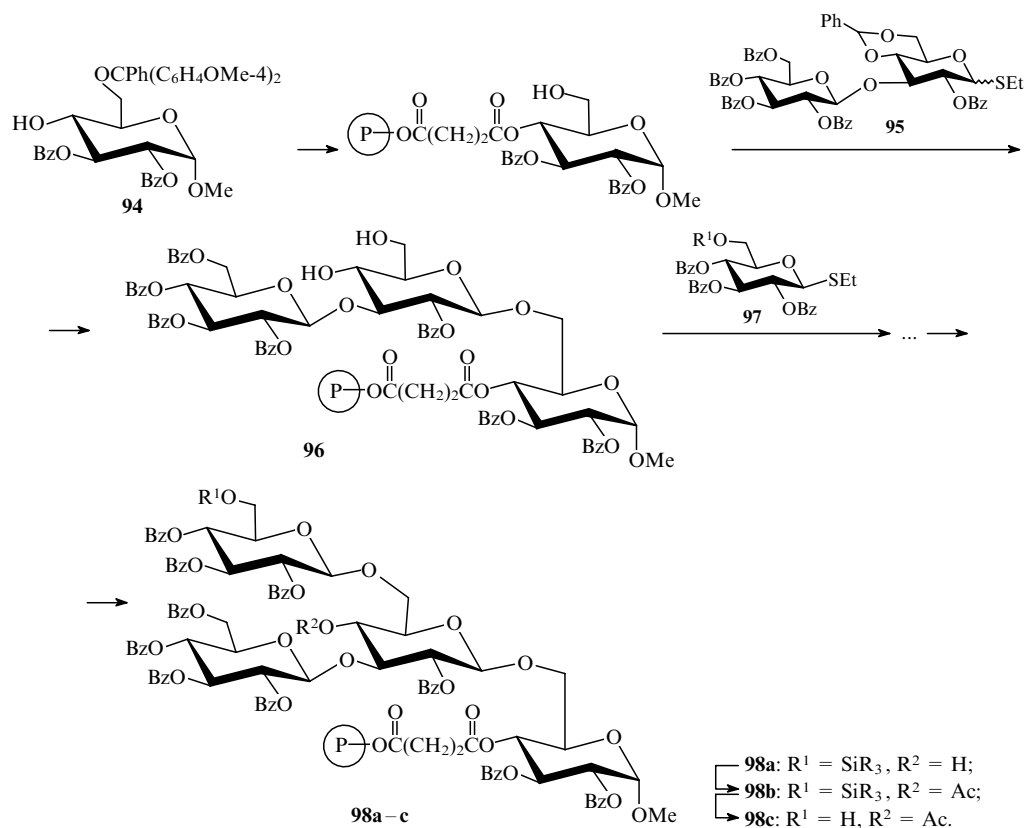
where the regio- and stereospecificity of the glycosidic bonds formed are determined by the specificities of glycosyl transferases.

The synthesis of the phytoalexin elicitor (PAE), which prevents viral and bacterial infections in plants, is yet another example of successful application of the solid-phase methodology in directed synthesis of biologically active and structurally complex oligosaccharides. Synthetic PAE (a branched heptasaccharide) presents substantial practical interest for agriculture, since the natural product is difficultly accessible due to its low concentration in plants. The synthesis of PAE **93** was carried out using two different approaches.

In the first approach (Scheme 19),⁵⁰ the oligosaccharide chain was elongated by sequential addition of blocks on a soluble polymeric support (PEG) using a thioglycoside glycosylation method. The starting monosaccharide, viz., methyl 2,3-di-*O*-benzoyl-6-*O*-dimethoxytrityl- α -D-glucopyranoside (**94**), was attached to the polymer modified with succinic acid through the hydroxy group at C(4) (the support loading was 148 mmol g⁻¹). After mild acidolysis of the dimethoxytrityl group, the polymer was introduced into the reaction with the disaccharide thioglycoside **95** in the presence of *N*-iodosuccinimide and trifluoromethanesulfonic acid. Benzylidene protection was removed by acid hydrolysis after which the immobilised trisaccharide **96** was subjected to regioselective glycosylation with the thioglycoside **97** at O(6'). Subsequent acylation of the hydroxy group at C(4')



Scheme 19



(**98a** → **98b**) and removal of silyl protection resulted in the tetrasaccharide **98c**.

Reiteration of this reaction sequence, *viz.*, the reaction with the disaccharide **95**, debenzilylation and the reaction with the thioglycoside **97**, afforded the protected immobilised heptasaccharide. Purification of the reaction products formed in each step from excess of the soluble reagents was achieved by precipitation of the polymeric material and subsequent washing with diethyl ether. Deprotection by treatment with sodium methoxide was accompanied by splitting of the heptasaccharide from the polymer eventually resulting in the biologically active PAE methyl glycoside (yield 18%).

According to the second scheme, PAE and its lower analogues were synthesised on a hydroxylated polystyrene resin using a photosensitive linker **99** and thioglycoside glycosylation.⁷ Nitrobenzyl alcohol **99** was glycosylated with phenyl-2,3,4-tri-*O*-benzoyl-6-*O*-(*tert*-butyldiphenylsilyl)-1-thio-β-D-glucopyranoside (**100**), and the resulting glycoside was immobilised. This glucose residue served as the origin of the oligosaccharide chain which was elongated by successive treatment with the thioglucosides **100**, **101** and **102** (Scheme 20). The thioglucoside **100** contained a selectively removable *tert*-butyldiphenylsilyl protecting group at O(6), while the thioglucoside **101** contained a 9-fluorenylmethoxycarbonyl (Fmoc) group at O(4). These groups were selectively removed when required, and the hydroxy groups liberated were glycosylated with the corresponding thioglucoside in the presence of dimethyl(methylthio)sulfonium triflate. The resulting heptasaccharide (overall yield 20%) was split off the support by photolysis.

Solid-phase synthesis was also used for the preparation of oligosaccharides containing 6-deoxy- and/or 2,6-dideoxymonosaccharide units which represent carbohydrate chains of some antibiotics.⁹ This synthesis combines ingeniously detachment of the oligosaccharide from the support with nucleophilic substitution of the hydroxy group involved in immobilisation of the sugar on the polymer. The Merrifield's resin modified by introduction of ethanesulfonic acid was used as the solid support. Methyl 4-*O*-

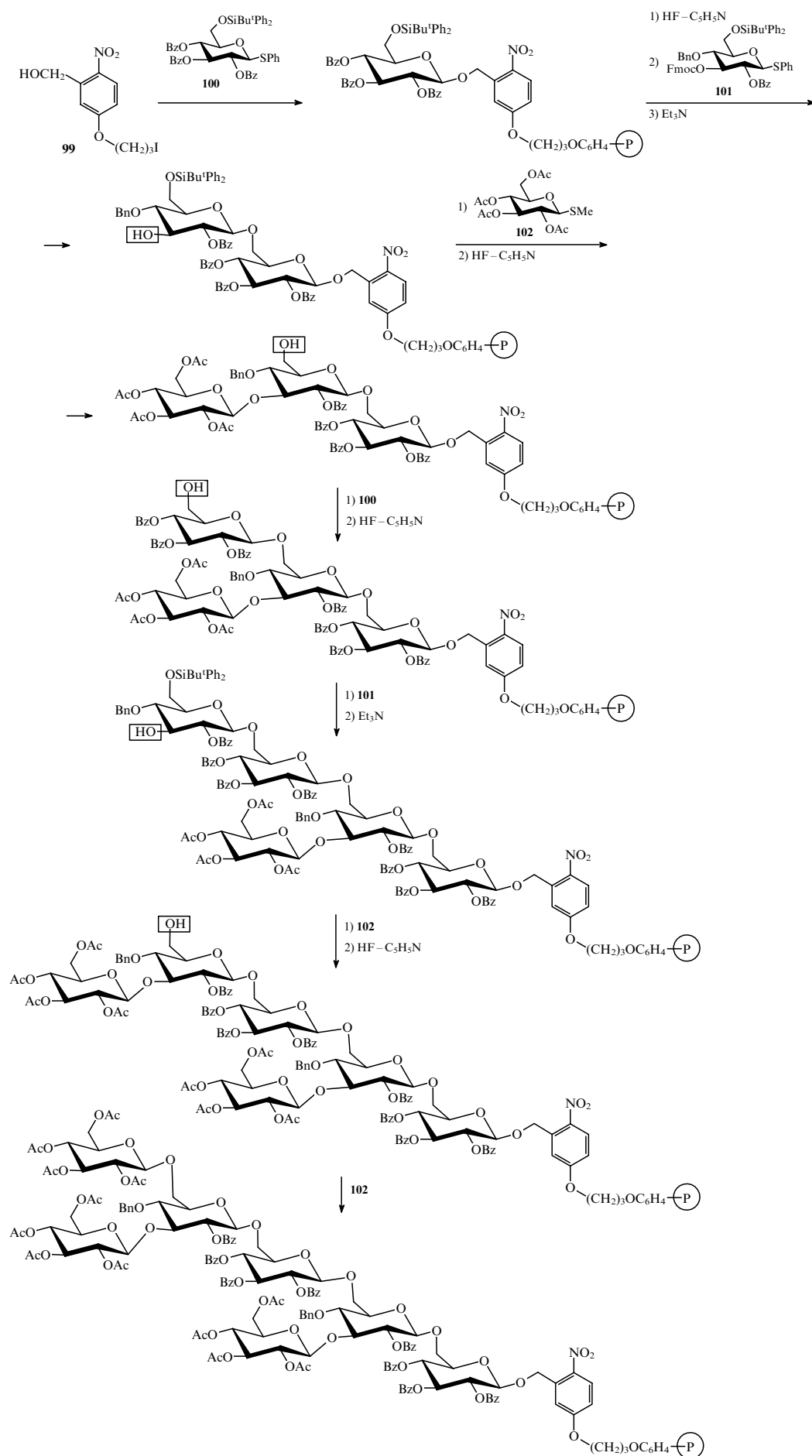
acetyl-2,3-di-*O*-benzyl- and methyl 2-*O*-acetyl-3,4-di-*O*-benzyl-α-D-glucopyranoside **103a(b)** were immobilised on this polymer (Scheme 21) after which *O*-acetyl groups were removed by treatment with guanidine. The immobilised monosaccharides **104a(b)** reacted with the glycosyl donors **105** and **106** in the presence of trimethylsilyl triflate to afford the corresponding immobilised disaccharides **107**–**110**. These disaccharides were split off the support by treatment with NaI in ethyl methyl ketone with simultaneous substitution of iodine for the sulfonyloxy group. The yields of iododeoxysaccharides (**111**–**114**) varied from 85% to 91%. Their treatment with Bu₃SnH gave the corresponding deoxy sugars **115**–**118** in 92% yield.

This method was used in the targeted synthesis of the carbohydrate fragment of the antibiotic olivomycin A (Scheme 22).⁹ Glucal **119** was immobilised on a sulfonylethylated Merrifield's polymer after which it was desilylated and treated with trichloroacetimidate **122**. The immobilised disaccharide **123** formed was desilylated (**123** → **124**) and glycosylated with glycosyl acetate **106** in the presence of trimethylsilyl triflate. The trisaccharide **125** was detached from the polymer with simultaneous substitution of iodine for bromine (yield 67%). The glycal **125** was used for direct incorporation of the carbohydrate fragment into the aglycon of olivomycin A.

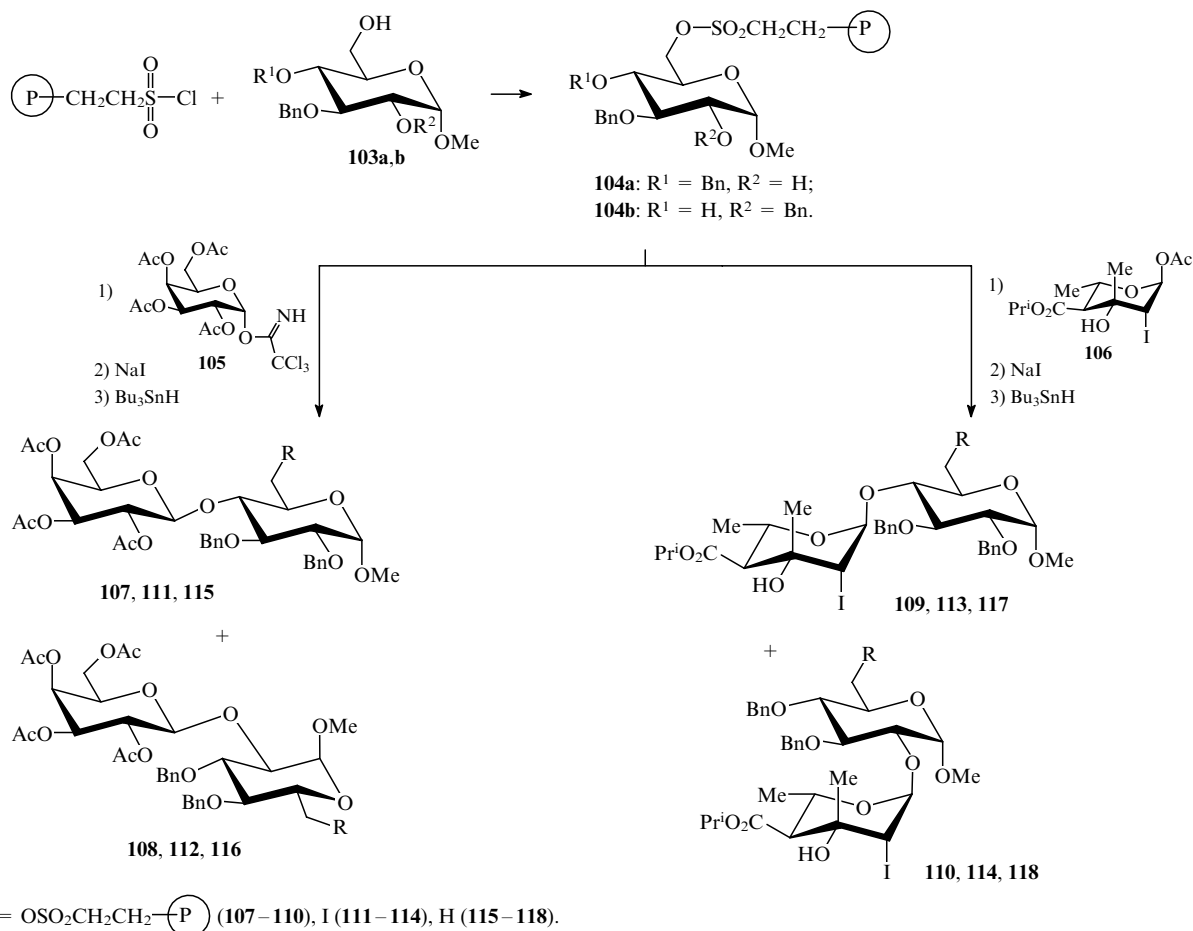
An important observation which awaits rationalisation is the fact that the glycosylation of the immobilised acceptor with trichloroacetimidate **122** was stereospecific leading exclusively to β-linkages, whereas the product synthesised in solution contained some proportion of α-linked oligosaccharide.

This example is also interesting in that it illustrates that the solid-phase synthesis of carbohydrates can be combined with simultaneous transformation of the monosaccharide residues. This significantly extends the range of reactions in synthetic chemistry of carbohydrates performed on solid supports. The same approach can be used for the introduction of amino sugar units into oligosaccharides if sodium azide is employed instead of NaI for splitting off the reaction product.⁹

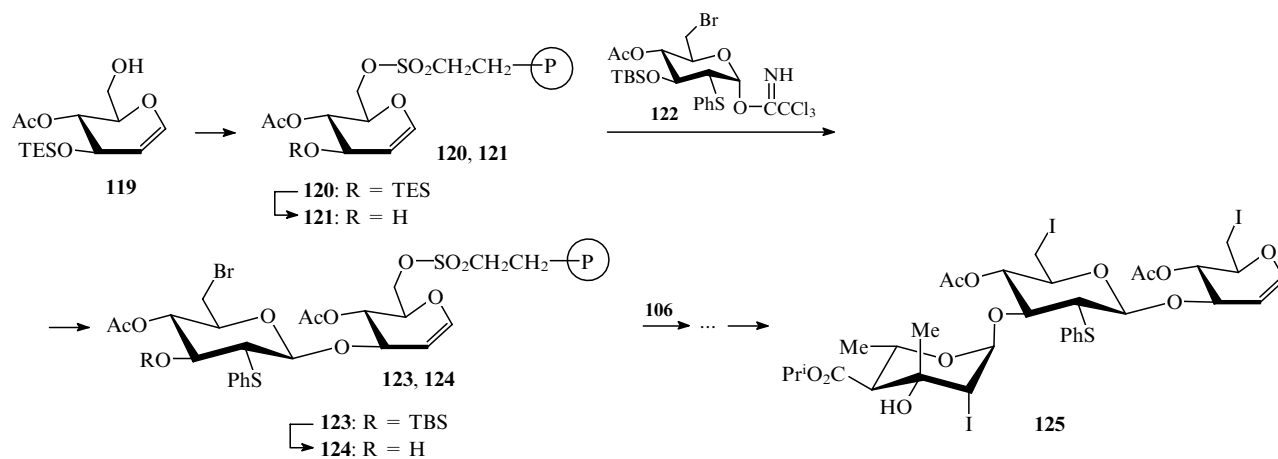
Scheme 20



Scheme 21



Scheme 22



TES = Et_3Si ; TBS = Bu_3Si .

V. Synthesis of glycopeptides

Glycopeptides are compounds in which oligosaccharides are covalently linked to amino acids or peptides by *O*- or *N*-glycosidic bonds. They are structural components of glycoproteins, the important naturally occurring glycoconjugates responsible for a great diversity of vital cell functions and are used as the simplest models in studies of biological activities of glycoproteins. In recent years, glycopeptides have acquired considerable practical importance, since many of them served as the basis for the development of new generations of highly efficient drugs.

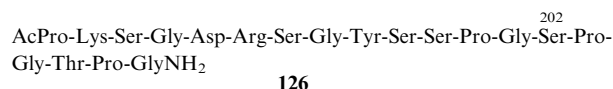
Glycopeptides are most commonly prepared by solid-phase synthesis, since their synthesis in solution faces serious problems.

Synthesis of glycopeptides can be performed by elongation of a peptide or an oligosaccharide chain. Those peptides in which an amino acid is glycosylated with a monosaccharide are the simplest representatives of the glycopeptide family.[¶] These can be prepared by direct glycosylation of the corresponding amino acid residue in a presynthesised immobilised peptide chain.[†]

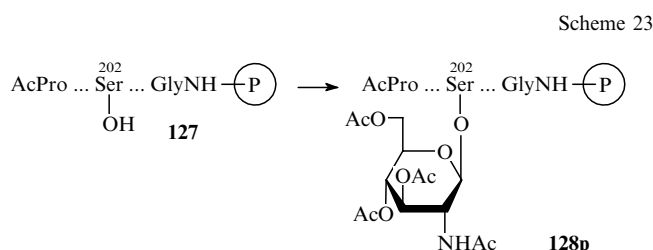
[¶] It is interesting to note that the mode of incorporation of the first monosaccharide residue is a crucial factor which determines the physicochemical characteristics of these peptides.

[†] For direct *O*-glycosylation of peptides containing serine and threonine residues in solution, see Refs 51 and 52.

This method has been briefly described by Hollósi *et al.*⁵³ in the example of the synthesis of a glycosylated fragment 189–207 of tau-protein (**126**), responsible for a certain stage of Alzheimer's disease, and of its simplified analogue.



The immobilised 19-membered peptide **127** possessing the necessary protecting groups in its amino acid residues (with the exception of the hydroxy group of serine-202 which was subject to glycosylation) was prepared by solid-phase peptide synthesis. This peptide was treated with 3,4,6-tri-*O*-acetyl-2-methyl-*D*-gluco-oxazoline[‡] prepared by treatment of per-*O*-acetyl- β -D-glucosamine with trimethylsilyl triflate as described in Ref. 54 (Scheme 23).



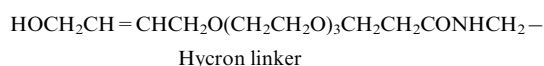
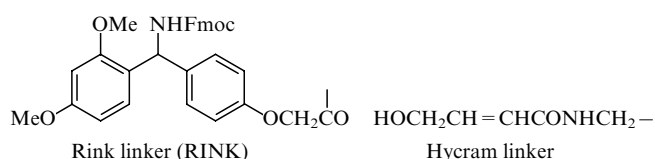
The resulting *O*-glycopeptide **128p** (yield 23%) was split off the polymer by treatment with a trifluoroacetic acid–anisole mixture and purified by chromatography. The structure of the glycopeptide **128** was confirmed by mass spectrometry. The glycosylation of the serine residue in its simple peptide analogue AcGly-Ser-Pro-Val-Glu-Lys was carried out in a similar way. The corresponding *O*-glycopeptide was obtained in 33% yield. This synthesis demonstrated the possibility of glycosylation of the serine residue adjacent to the proline residue of immobilised peptides, which normally hardly undergoes glycosylation.

The synthesis of *N*-glycopeptides in which mono- and oligosaccharide residues (including hexasaccharides) are linked to the asparagine residue of the hexapeptide Asn-Tyr-Gly-Phe-Leu by an *N*-glycosidic bond is yet another example of direct glycosylation. In this synthesis, the hexapeptide with *N*-terminal aspartic acid was immobilised on a support and the aspartic acid was converted into the pentafluorophenyl ester. The activated ester was brought into reaction with the corresponding glycosylamines in the presence of hydroxybenzotriazole and amine to afford *N*-glycosylasparagines.⁵⁵

It is necessary to note that direct glycosylation of immobilised peptide chains has not received wide recognition in synthetic practice. It is the classical solid-phase peptide synthesis (see, *e.g.*, Refs 56–90) that is mainly employed for the preparation of glycopeptides bearing a monosaccharide residue or a short oligosaccharide chain, which makes use of the corresponding glycosylated amino acids.

However, implementation of solid-phase glycopeptide synthesis in an automated regime of conventional peptide synthesis required that a number of problems was solved, such as a search for supports and linkers providing both the optimum conditions for the condensation in the elongation of the peptide chain and smooth non-destructive liberation of the target glycopeptide from the support. The most common support is Merrifield's peptide resin⁵⁶ modified by incorporation of benzyl alcohol fragments ($\text{HOCH}_2\text{C}_6\text{H}_4\text{OCH}_2-\text{P}$),⁵⁸ the role of linker is played by a compound with benzhydrylamine and phenoxyacetic acid fragment (the so-called Rink linker),⁶¹ a variety of compounds

containing β -hydroxyallylic groups (Hycron and Hycram linkers)^{62, 63} and nitrobenzophenone oxime.⁶⁵

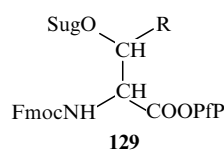


In parallel with a search for linkers, the general strategy of glycopeptide synthesis required unification of procedures used for incorporation of glycosylated amino acids into the peptide chain.

To this end, efficient methods for incorporation of glycosylated amino acid residues into the peptide chain have been developed and synthesis of such fragments has been proposed.[§]

And, finally, particular attention has been paid to the protection of hydroxy groups of carbohydrates and functional groups of amino acids as well as to protecting group introduction, removal and manipulations as required in the synthesis.

The Fmoc/PfP strategy was found to be the most efficient in the synthesis of *O*-glycopeptides. In this case, the amino group of serine or threonine (**129**) derivatives is protected with a Fmoc group which is easily removed upon treatment with mild bases, while the carboxy group is activated by conversion into the pentafluorophenyl ester (PfP).



R = H, Me.

The use of these derivatives allows incorporation of glycosylated amino acids into the peptide chain in an automated mode of a conventional peptide synthesis.

An alternative approach to the synthesis of glycopeptides with a complex carbohydrate chain consists in the elongation of the oligosaccharide chain starting from the monosaccharide residue that has been incorporated into the immobilised peptide chain. In this case, as in the oligosaccharide synthesis in solution, the choice of protecting groups in the monosaccharide residues and the method of glycosylation which provide the highest regio- and stereoselectivity of glycosylation are of great importance. A factor which largely determines the successful outcome of the glycopeptide synthesis is the proper choice of a support which ensures effective synthesis of both peptide and oligosaccharide fragments within a single system '(support + linker)–solvent'. The conditions for the peptide and oligosaccharide syntheses can differ (*e.g.*, the synthesis of an oligosaccharide fragment should preclude the presence of water or any other hydroxyl-containing components), which may require additional technical manipulations connected with a change of solvents in the course of the synthesis.

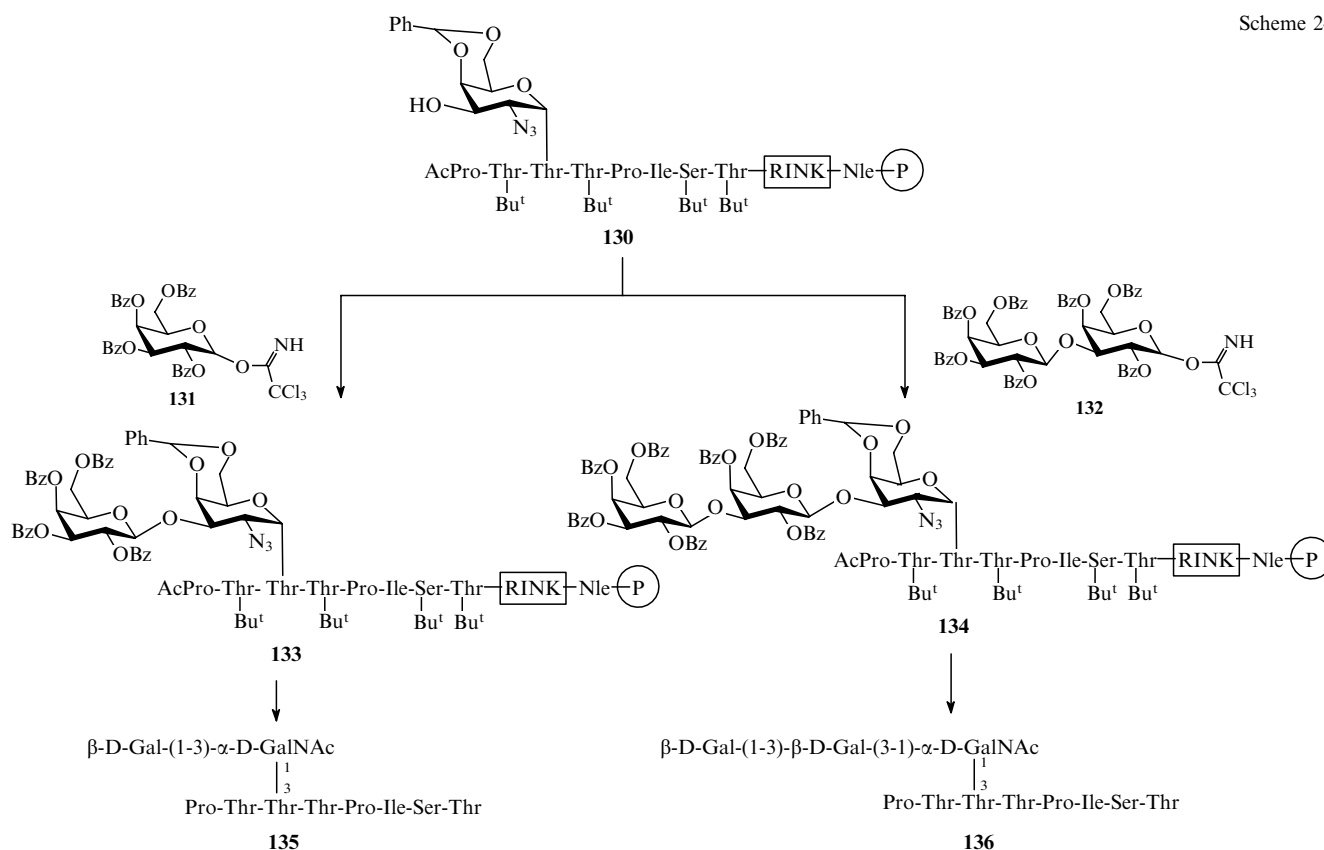
Glycopeptide syntheses by chemical elongation of the oligosaccharide chain was described in detail in a fundamental study by Paulsen *et al.*⁹¹

The Rink linker and norleucine (Nle) as the internal standard were used in the synthesis of mucin core fragments, *viz.*, glycopeptides with the peptide chain comprising eight amino acids and a di- or a trisaccharide residue (Scheme 24). One of the threonine residues incorporated into the peptide chain immobilised on a

‡ An attempt to incorporate the first monosaccharide into an immobilised peptide by direct glycosylation with sugar trichloroacetimidates was unsuccessful.

§ These residues include *O*-glycosylated threonine and serine residues in the case of *O*-glycopeptide synthesis and *N*-glycosylated asparagine in the case of *N*-glycopeptide synthesis.

Scheme 24



PEGA support contained a substituted 2-azido-2-deoxy- α -D-galactose residue linked by an *O*-glycosidic bond. The only free hydroxy group at the C(3) atom of the sugar residue in this immobilised glycopeptide (**130**) was glycosylated with the corresponding *O*-glycosyl trichloroacetimidates. As was noted above, this method is used for the formation of β -glycosidic linkages in good yields and with high stereoselectivity. Thus, the reaction of the glycopeptide **130** with *O*-(tetra-*O*-benzoyl-D-galactopyranosyl)- (**131**) and *O*-(perbenzoyl- β -D-galactopyranosyl-(1-3)-D-galactopyranosyl) trichloroacetimidates (**132**) in the presence of trimethylsilyl triflate afforded the glycopeptide derivatives **133** and **134**, respectively. The latter were split off the support with trifluoroacetic acid (yields 67% and 33%, respectively), this was accompanied by removal of *O*-*tert*-butyl protecting groups. The azido groups in the resulting compounds were transformed into acetamido groups with subsequent removal of *O*-benzoyl protection. This procedure afforded the glycopeptides **135** and **136** with the *N*-acetylgalactosamine residue in the carbohydrate-peptide linkage site.

An attempt to perform this synthesis on other supports and substitution of acetyl groups in the trichloroacetimidates **131** and **132** for *O*-benzoyl groups decreased the yields of the resulting glycopeptides **133** and **134**.

The same linker and the support were used in the synthesis of a series of isomeric glycopeptides with (1-3) and (1-6) glycosidic linkages. The starting monoglycosylated peptide comprised a threonine residue glycosylated with 2-azido-2-deoxy-3,4-*O*-isopropylidene- α -D-galactopyranose (Scheme 25). The glycosylation of the peptide **137** with the trichloroacetimidates **131** and **132** gave the glycopeptide derivatives **138** and **139** (yields 69% and 53%, respectively) which were further converted into the corresponding *O*-glycopeptides after transformation of azido groups into acetamido groups with subsequent liberation from the support and deprotection.

This scheme was also used in the synthesis of *O*-glycopeptides having branched oligosaccharide chains. Here, the protecting benzylidene group in the immobilised glycopeptide **133** was

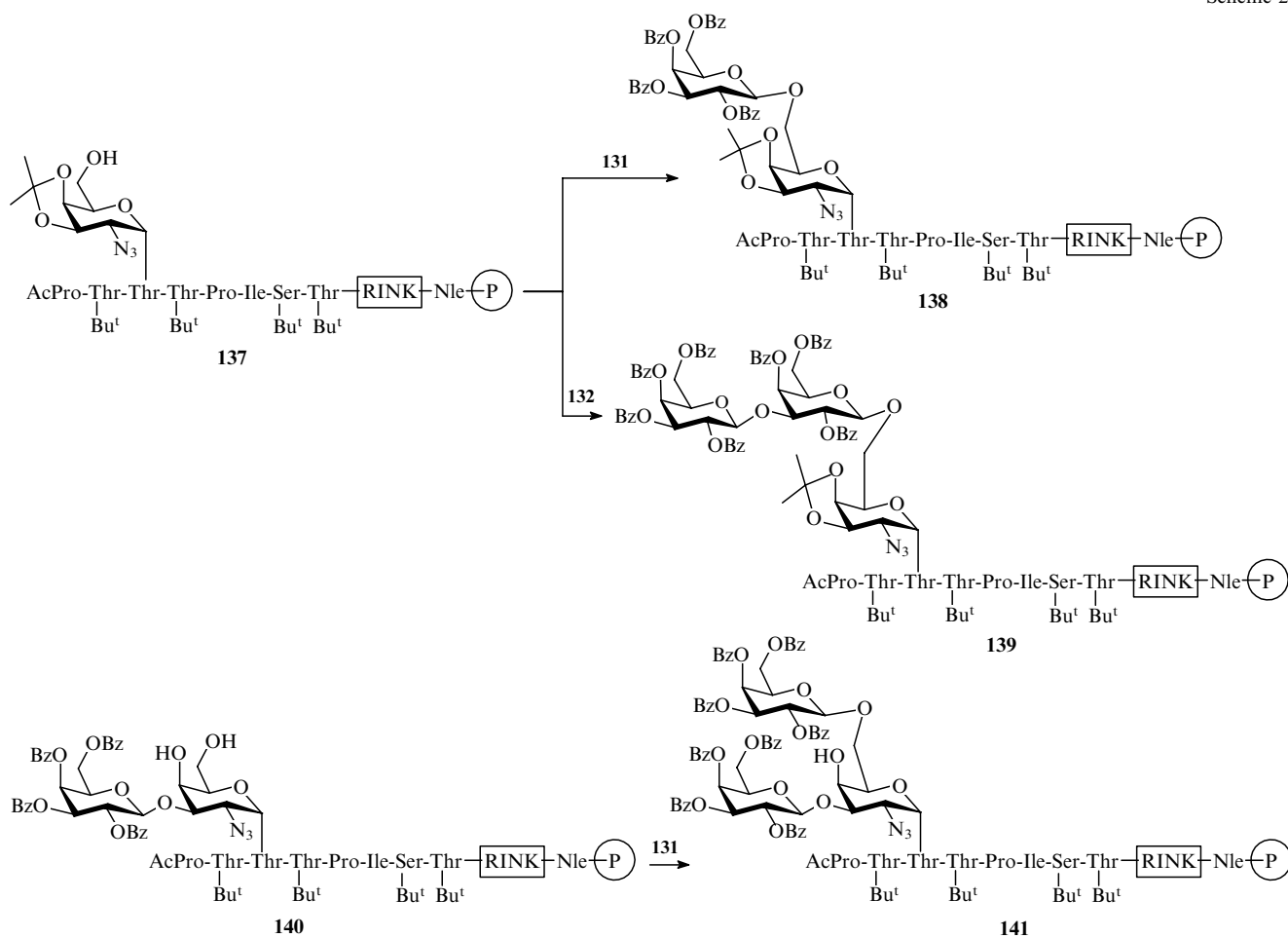
removed by mild acid hydrolysis, and the glycopeptide **140** was selectively glycosylated with the trichloroacetimidate **131** at the primary hydroxy group of the partially protected disaccharide fragment. This procedure afforded the glycopeptide **141** with a branched oligosaccharide chain.

This approach was also used in the preparation of glycopeptides with carbohydrate chains built of amino sugars. The immobilised glyconapeptides **142** and **143** structurally related to compounds **130** and **137** with an additional N-terminal glutamic acid residue were glycosylated with an excess of *O*-(3,4,6-tri-*O*-benzoyl-2-deoxy-2-trichloroethoxycarbonylamino- α -D-glucopyranosyl) trichloroacetimidate **144** (Scheme 26). The *N*-trichloroethoxycarbonylamino- and azido groups in the resulting glycopeptide derivatives **145** and **146** were transformed into *N*-acetylamino groups, the protecting groups in amino acid and sugar residues were removed after which the reaction products were split off the support. The corresponding glycopeptides, which represent mucin core fragments, were obtained in 62% yield.

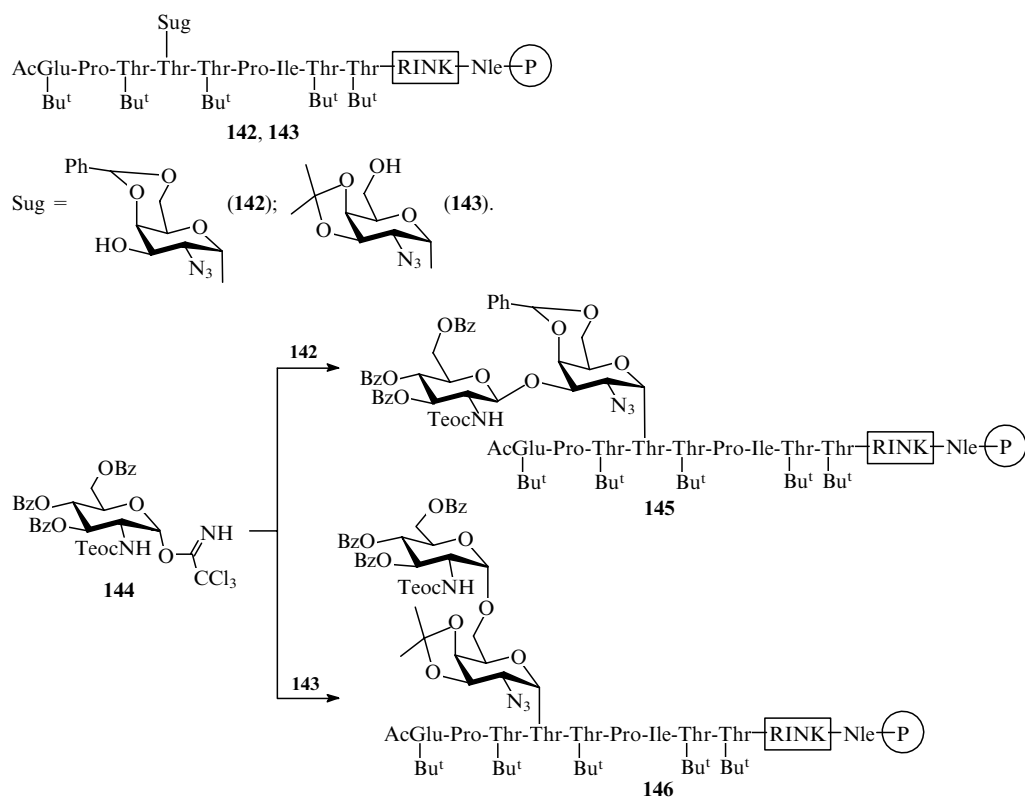
Obviously, the elongation of an oligosaccharide chain in an immobilised glycopeptide bearing a monosaccharide residue is a flexible and reliable, albeit labour-consuming, method for the synthesis of complex glycopeptides. This procedure can be considerably simplified if glycosylation is performed with the use of glycosyl transferases. The use of enzymes makes monosaccharide protection unnecessary and ensures high regio- and stereoselectivity in the formation of glycosidic bonds. The supports employed in enzymic glycopeptide synthesis involving consecutive elongation of peptide and oligosaccharide chains must provide adequate conditions both for the synthesis of the peptide chain and for the transfer of monosaccharide residues under the action of glycosyl transferases.[¶] This problem was successfully overcome

[¶] In choosing supports for such syntheses, one should take into account the fact that peptide syntheses are performed in organic solvents, while the elongation of the oligosaccharide chain is carried out in aqueous media.

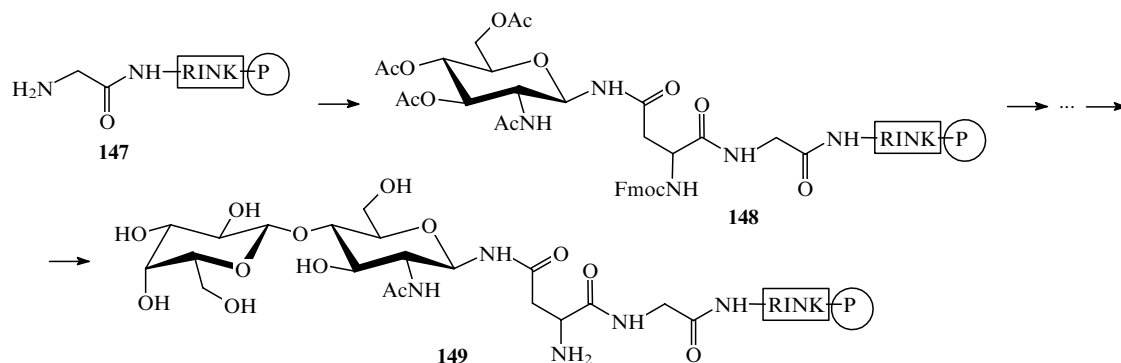
Scheme 25



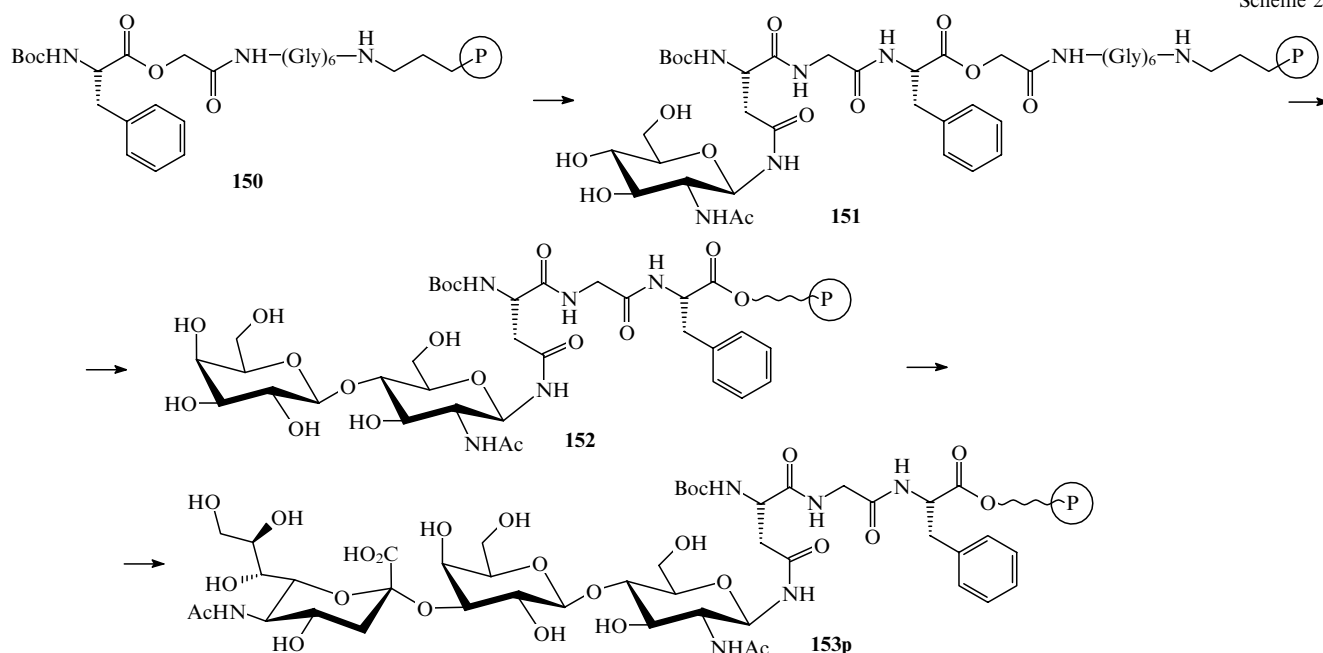
Scheme 26



Scheme 27



Scheme 28

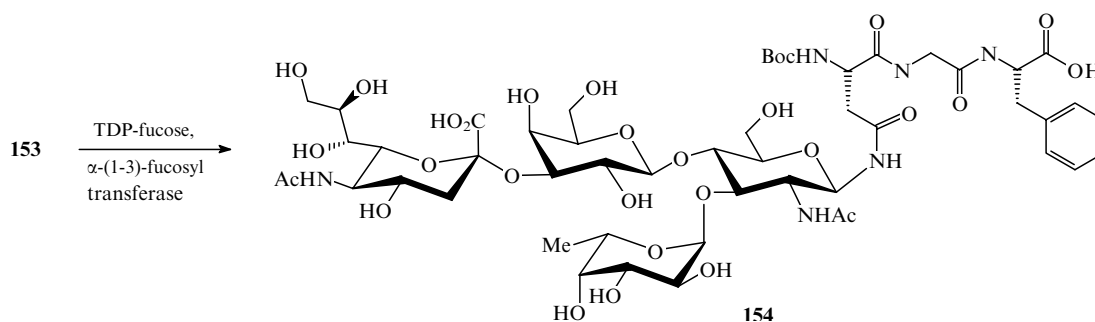


through the use of complex polymeric supports (PEGA) capable of swelling both in water and in organic solvents, or of mineral supports (*e.g.*, CPG modified by introduction of amino groups).

The synthesis of a model *N*-glycopeptide, *viz.*, { β -D-Galp-(1-4)- β -D-GlcNAc-[1-N(4)]-Asn-Gly, on a PEGA-type support modified by attachment of the Rink linker is shown in Scheme 27.¹⁸ A C-terminal amino acid, *viz.*, *N*-Fmoc-glycine, was immobilised on a modified support. After removal of the Fmoc-group, the immobilised glycine **147** was made to react with *N*(4)-glycosylated *N*(2)-Fmoc-asparagine to give the glycopeptide **148**. Incubation with UDPGal and β -(1-4)galactosyl transferase was carried out after removal of Fmoc- and *O*-acetyl protecting groups. The resulting glycopeptide **149** was split off the polymer with CF₃COOH or used further in the immobilised form. The glycosylation reaction was monitored by ¹H NMR spectroscopy.

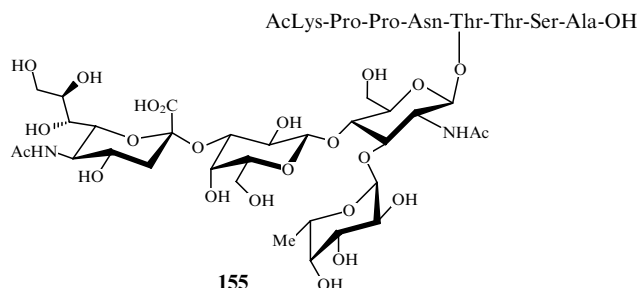
The use of CPG modified with 3-aminopropyl groups for solid-phase chemo-enzymic synthesis of glycopeptides was exem-

plified in the preparation of sialyl-Lewis-X glycopeptide (Scheme 28).¹⁴ In this synthesis, the hexaglycin fragment was attached to the amino groups of the modified CPG; the unreacted amino groups of the polymer were 'capped' by acetylation to prevent their involvement in further reactions after which the terminal amino group of the hexapeptide was acetylated with *O*-(*N*-Boc-phenylalanyl)glycolic acid. The ester bond formed is susceptible to hydrolysis with chymotrypsin and is well-suited for splitting the reaction product off the support. Following liberation of the amino group in the ester **150**, glycine and *N*(4)-glycosylated asparagine residues were introduced by conventional methods of solid-phase peptide synthesis. The immobilised glycopeptide **151** was incubated with UDPGal and β -(1-4)-galactosyl transferase to afford the immobilised glycopeptide **152**. The latter was made to react with cytidine 5'-phospho-*N*-acetylneuraminic acid (CMP-*N*-acetylneuraminic acid, the activated form of *N*-acetylneuraminic acid) and α -(2-3)-sialyl transferase to yield the



glycopeptide **153p** containing a trisaccharide chain. The latter is easily split off the support with α -chymotrypsin. After liberation, the *N*-glycopeptide **153** was further glycosylated in solution with thymidine 5'-diphospho-L-fucose (TDP-fucose) in the presence of α -(1-3)-fucosyl transferase eventually resulting in the branched *N*-glycopeptide **154**.

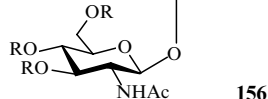
The synthesis of a more complex biologically important *O*-glycopeptide **155** with the same tetrasaccharide moiety, which represents a fragment of the mucin-type glycoprotein MAdCAM-1 (a specific ligand for selectins),⁹² was carried out in a similar way. The problems which arose in its synthesis were connected with the high lability of the *O*-glycosidic bond between *N*-acetylglucosamine and threonine.



The synthesis of the glycopeptide **155** was carried out on PEGA and CPG modified with aminopropyl groups. CPG appeared to be more convenient than organic supports of the PEGA type. The Hycron linker containing an allylic hydroxy group with an attached *N*-Fmoc-alanine as a terminal amino acid was used for the immobilisation of the peptide chain.

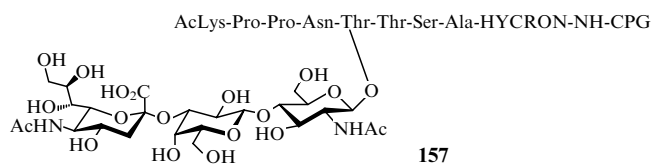
After removal of the Fmoc-group in the polymer Fmoc-Ala-HYCron-NH-CPG, the peptide chain was elongated from the alanine residue using a standard *N*-Boc/OBu^t procedure. *N*-Acetylglucosamine linked to threonine served as a carbohydrate-peptide junction. After removal of *N*- and *O*-protecting acid-labile groups (treatment with trifluoroacetic acid in the presence of ethanedithiol) from the immobilised monoglycosyloctapeptide **156**, this

AcLys(Boc)-Pro-Pro-Asn(Trt)-Thr-Thr(Bu^t)-Ser(Bu^t)-Ala-HYCron-NH-CPG



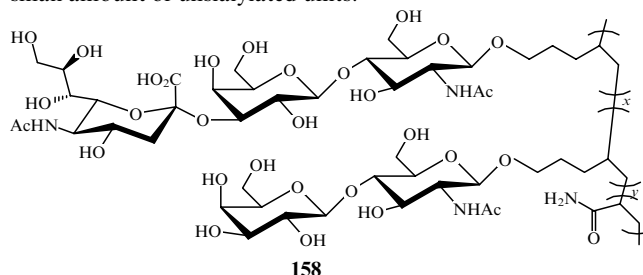
was incubated first with UDPGal in the presence of galactosyl transferase and then with CMP-*N*-acetylneuraminic acid in the presence of α -(2-3)-sialyl transferase. The resulting triglycosyl peptide derivative **157** was split off the support in the presence of

Pd(0) as a catalyst. The yield of the glycopeptide **157** was 9% with respect to the immobilised alanine. The glycopeptide **157** was converted into the glycopeptide **155** by enzymic fucosylation as described above.

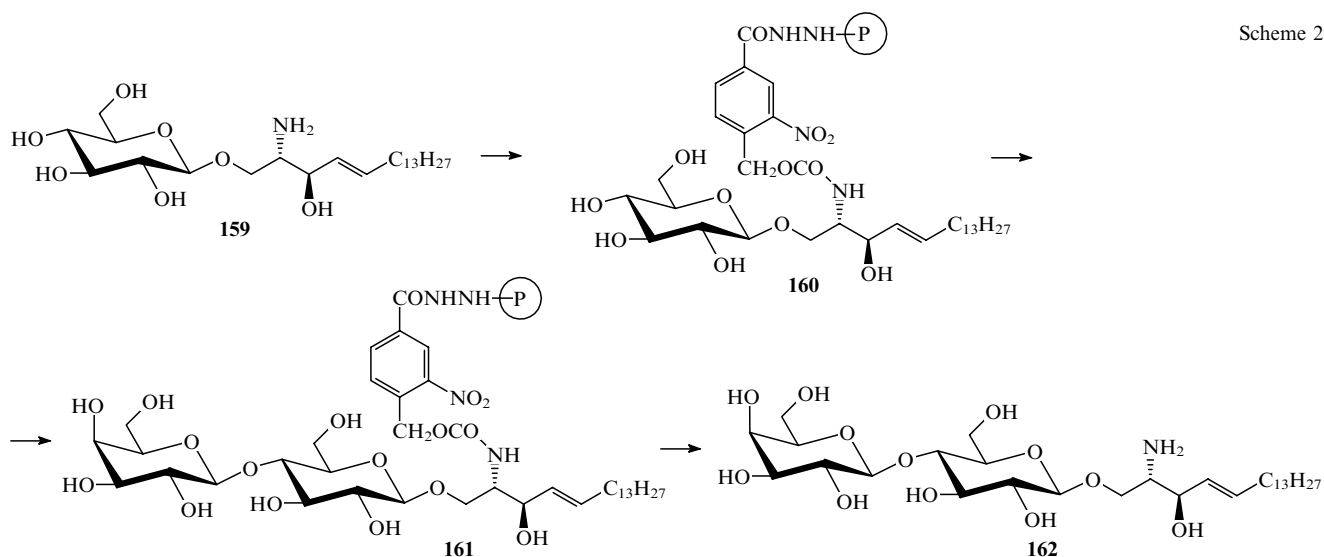


The glycopeptide **155** has also been synthesised in a solution. The yield of the target product was higher in this case, but the reaction time increased significantly (up to 9 days). In the authors' opinion,⁹² the shorter duration of solid-phase synthesis may fully compensate for the lower yields of the target product.

The enzymic elongation of oligosaccharide chains was also employed in the synthesis of glycoconjugates which are used in the manufacture of diagnostic preparations (artificial antigens), *e.g.*, in the synthesis of a polymer containing the α -NeuNAc(2-3)- β -D-Galp(1-4)- β -D-GlcNAc chains attached to a polyacrylamide carrier.⁹³ The polyacrylamide carrying monosaccharide residues was obtained by copolymerisation of *n*-pent-4-enyl 2-acetamido-2-deoxy- β -D-glucopyranoside and acrylamide.⁹⁴ This was incubated consecutively with UDPGal in the presence of β -(1-4)galactosyl transferase and *p*-nitrophenyl *N*-acetylneuraminic acid in the presence of Tc-Ts-transsialidase to afford the synthetic glycoconjugate **158**, which contained trisaccharide units together with a small amount of unsialylated units.



Thus, in some cases the solid-phase synthesis is confined exclusively to the preparation of a glycopeptide containing only one monosaccharide residue in the carbohydrate-protein junction, which is followed by enzymic elongation of the carbohydrate chain in solution. The synthesis of a large series of *N*-glycopeptides the chains of which contained different amino acid sequences including two asparagine residues glycosylated with *N*-acetylglucosamine, *N*-acetylglucosamine and sialyl(2-6)-*N*-acetylglucosamine, provides an example.⁹⁵



The solid-phase synthesis of lactosylceramide on a soluble support with a photosensitive linker is yet another, thus far unique example of enzymic elongation of a carbohydrate chain in glycolipids.⁹⁶ Synthetic (2*S*,3*R*,4*E*)-2-amino-1-(β -D-glucopyranosyloxy)-3-hydroxyoctadec-4-ene (**159**, glucosylsphingosine) was converted into a urethane (4-hydroxymethyl-3-nitrobenzoic acid derivative) and immobilised on a copolymer of acrylamide with *N*-acryloyloxysuccinimide (Scheme 29). The immobilised glycolipid **160** was incubated with UDPGal and galactosyl transferase. The resulting disaccharide derivative **161** was purified from low-molecular-weight admixtures by dialysis and the reaction product **162** was split off the polymer by photolysis.

VI. Synthesis of phosphoglycans

Solid-phase synthesis has successfully been used for the preparation of fragments of phosphoglycans, *i.e.*, the regular biopolymers built of repeating carbohydrate units linked through phosphodiester bonds. This class of biopolymers, *e.g.*, teichoic acids, are widespread in microorganisms where they play the role of antigens.

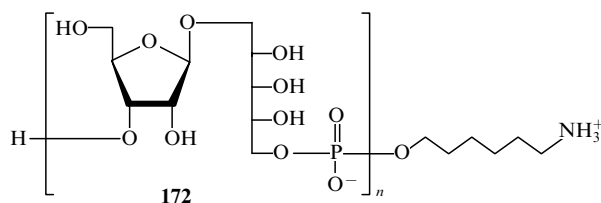
Synthesis of phosphoglycans in solution results exclusively in low-molecular-weight compounds which contain no more than two or three repeating units of the biopolymer. Apparently, solid-phase synthesis is more preferable in the preparation of high-molecular-weight phosphoglycan fragments. Several examples of such syntheses are currently known.

In general, the synthesis of phosphoglycans is very close to the synthesis of polynucleotides and differs in the structure of the repeating units which incorporate more or less complex carbohydrate structures.

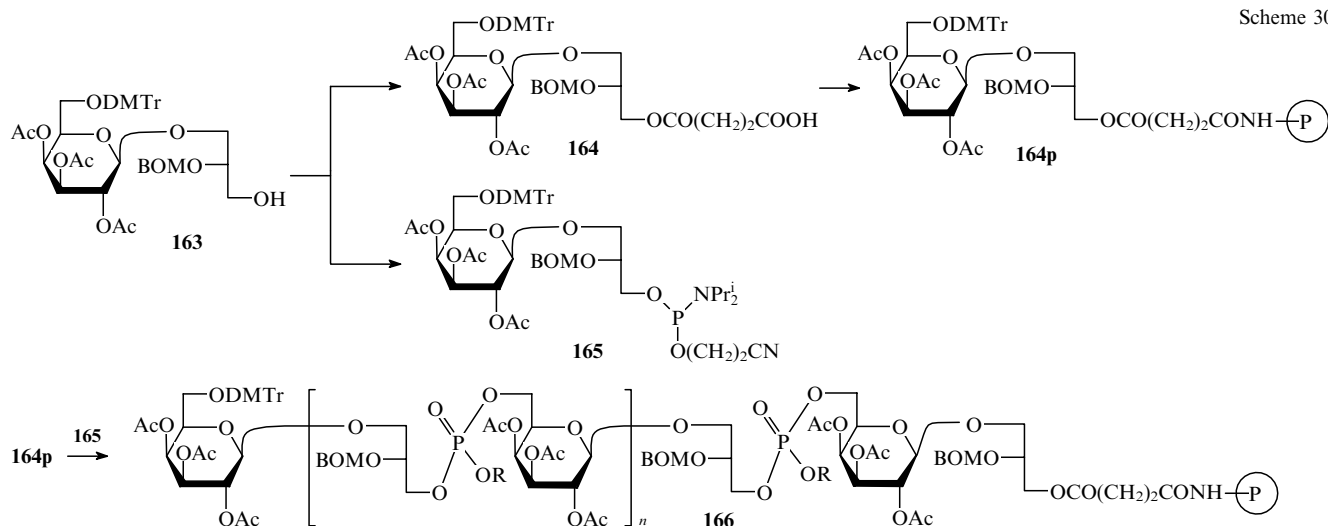
The synthesis of a fragment of teichoic acid from *Bacillus licheniformis* is the first example of solid-phase phosphoglycan synthesis. This biopolymer is built of 1-*O*-(β -D-galactopyranosyl)glycerol repeating units linked *via* (6'-3)-phosphodiester bonds. The solid-phase synthesis of the trimer of the repeating unit of this phosphoglycan was performed on a modified CPG; the phosphodiester bond was formed using the phosphoramidite method (Scheme 30).⁹⁷ The galactopyranosylglycerol derivative **163**, which represents a fragment of the repeating unit of this biopolymer, was synthesised in solution and was treated with succinic anhydride to yield the succinic acid monoester **164**, which was then immobilised on the modified CPG. The reaction of the derivative **163** with $\text{Pr}_2\text{NP}(\text{OCH}_2\text{CH}_2\text{CN})\text{Cl}$ gave (galactosylglyceryl) (2-cyanoethyl) *N,N*-diisopropylphosphoramidite **165**, which was used as a phosphorylating agent. The elongation of the oligomeric chain was carried out in an automated mode using

a well-established technique for the synthesis of oligonucleotides. This included reiteration of the following operations: liberation of the primary hydroxy group in the galactose residue of the polymer **164p** by removal of the 6'-dimethoxytrityl group, the reaction with phosphoramidite **165** in the presence of 1*H*-tetrazole, acetylation of unreacted free hydroxy groups in order to prevent their interaction at subsequent steps and oxidation of trivalent phosphorus into pentavalent phosphorus with iodine. The yield in each reaction cycle was 95%. The target product **166** ($n = 3$) was split off the support by ammonolysis with simultaneous removal of *O*-acetyl and cyanoethyl groups. The structure of the teichoic acid fragment thus prepared was confirmed by ¹H NMR spectroscopy and FAB-mass spectrometry.

The synthesis of a fragment of the capsular polysaccharide of *Haemophilus influenza* (type b), which is known to induce meningitis in children, proved to be more difficult. This synthesis was undertaken⁹⁸ with the aim of using this phosphoglycan as an artificial antigen in the preparation of a synthetic vaccine (Scheme 31). This synthesis utilised the methodology of the oligonucleotide synthesis and was carried out on a modified CPG. The substituted ribosylribitol **167** was used as the starting compound. The disiloxanedyl group was removed by treatment with Bu_4NF , the primary hydroxy group was selectively protected by silylation and the secondary hydroxy group at C(3') was converted into the succinic acid monoester. The resulting ester **168** was immobilised on CPG and detritylated to afford the polymer **169**. The ribosylribitol **167** was converted into 2-cyanoethyl *N,N*-diisopropyl phosphoramidite **170**. This was then introduced into reaction with the polymer **169**, which was carried out in an automated synthesiser under conditions of nucleotide synthesis. The reaction cycle was repeated as many times as required after which a (6-aminoethyl) phosphate spacer was attached to the oligomer **171** ($n = 6$) in order to ensure its further transformation into a synthetic antigen following binding to the protein. The reaction product was split off the support by



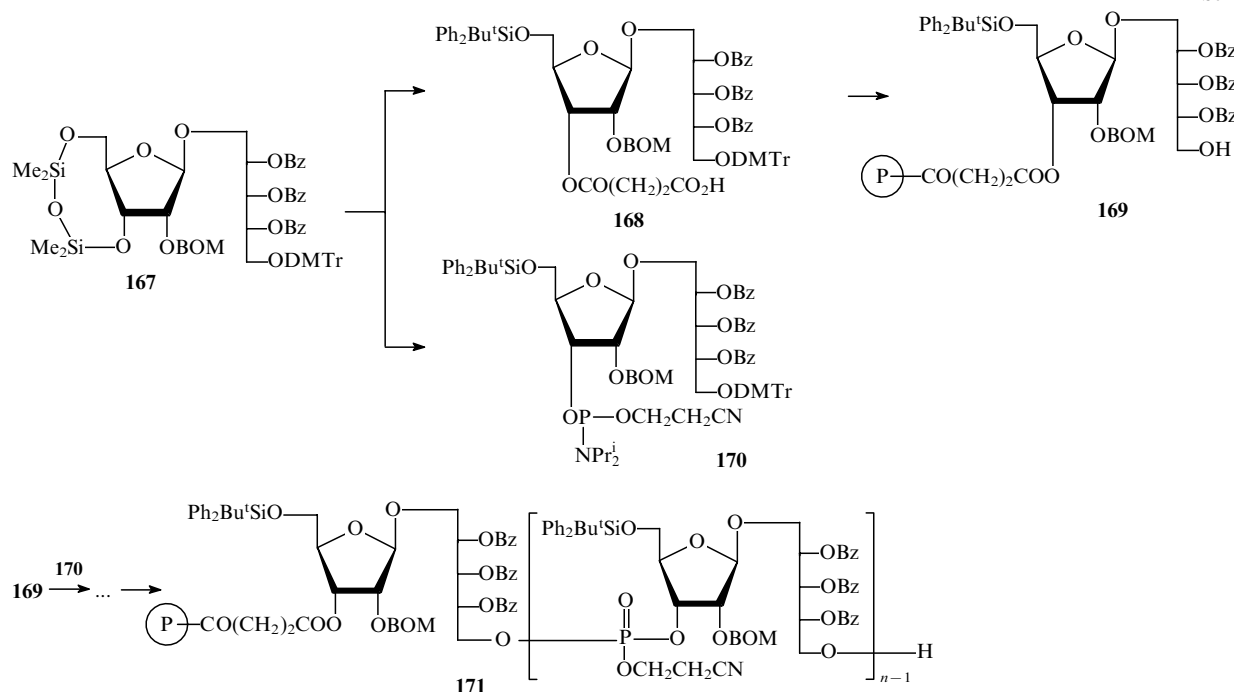
ammonolysis; the protecting groups were removed by treatment with Bu_4NF and hydrogenolysis. The overall yield of the target oligomer **172** ($n = 6$) was 24%.



DMTr is dimethoxytrityl; BOM is benzyloxymethyl.

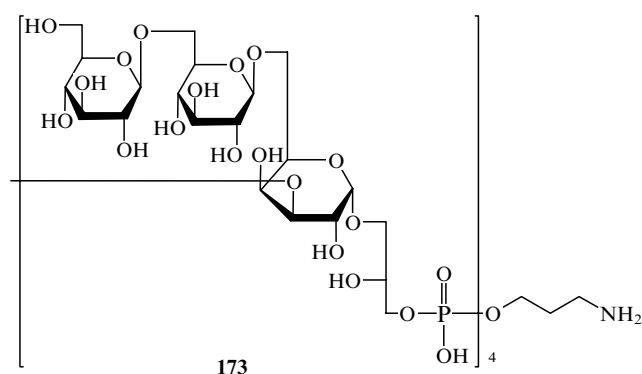
Scheme 30

Scheme 31

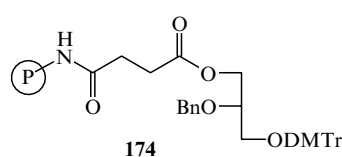


Synthesis of the phosphoglycan on a soluble support (PEGA)⁹⁹ using an analogous scheme with *O*-benzyl protection, was found to be more efficient and suitable for practical purposes. In this case, the loading of the support was larger (109 mmol g^{-1}) than in the previous synthesis (34 mmol g^{-1}); higher oligomers were synthesised in 35% yield.

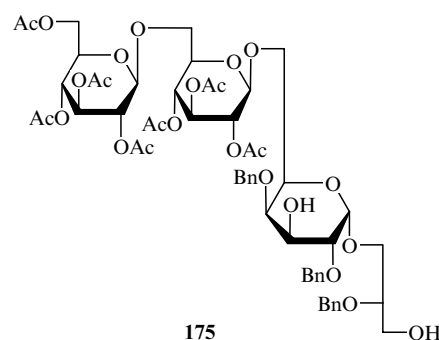
The same standard procedure was used in the synthesis¹⁰⁰ of a fragment **173** of the phosphoglycan of *Haemophilus pleuropneumoniae* (serotype 2) which induces swine diseases. This fragment is made up of β -D-glucopyranosyl-(1-6)- β -D-glucopyranosyl-(1-6)- α -D-galactopyranosyl-(1-3)-glycerol repeating units linked through (1-3')-phosphodiester bonds.



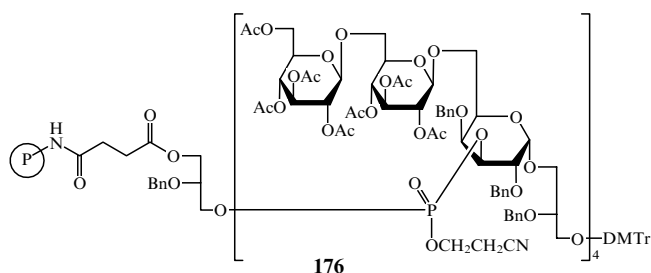
The synthesis of the tetrameric fragment of the repeating unit¹⁰⁰ was carried out according to a scheme similar to those used in previous syntheses. CPG modified with aminopropyl groups served as the support and the phosphoramidite method was employed for the formation of the phosphodiester bond.



2-*O*-Benzyl-3-*O*-dimethoxytritylglycerol was converted into a monoester of succinic acid and immobilised on CPG as in the previous syntheses. The resulting product **174** was detritylated and used as an initial unit for the elongation of the chain. The



primary hydroxy group in the glycerol portion of the repeating unit, viz., triglycosylglycerol **175**, was protected with dimethoxytrityl ether, and the hydroxy group at C(3) of the galactose residue was converted into (2-cyanoethyl) *N,N*-diethylphosphoramidite and used as a phosphorylating agent under conditions of automated oligonucleotide synthesis. The immobilised tetramer of the phosphoglycan repeating unit **176** obtained after four reaction cycles was detritylated with subsequent introduction of a phosphorylated spacer. The reaction product was split off the support by ammonolysis with simultaneous removal of protecting ester groups. Subsequent hydrogenolysis gave compound **173** which could be employed for the preparation of a synthetic vaccine.



These results demonstrate the high efficiency of the solid-phase synthesis of phosphoglycans of the teichoic acid type, which utilises well-established techniques of nucleotide synthesis.

VII. Conclusion

The examples of solid-phase carbohydrate syntheses described above demonstrate that advances in this area are modest yet. The problems encountered in solution synthesis of various carbohydrate structures are related to the polyfunctionality of monosaccharides and non-stereospecificity of the formation of glycosidic bonds; these problems persist and preclude automation of the synthesis.

It is quite natural that the 'technology' of solid-phase synthesis of carbohydrates demands further improvement and studies in this area are currently under way. It is desirable that the elongation of the carbohydrate chain by chemical methods should involve standard procedures for the formation of active glycosyl-donor function and for the liberation of hydroxy groups after each elongation step. The solution of this problem would open a way to the automation of the synthetic process.

An example of a successful solution of this problem is described in this review, particularly, in the section devoted to oligosaccharide synthesis by the glycal method. It should be noted that elongation of the oligosaccharide chain is more conveniently performed in the direction from the reducing end of the chain to its non-reducing end, since in this case the elongation of the chain by addition of the next fragment to the immobilised reagent should be preceded only by a selective liberation of the required hydroxy group, which is much easier to perform than to reconstruct the activated glycosidic centre.

Yet another problem which demands urgent solution is the choice of ideal polymeric supports and linkers compatible with them. Their wide availability will significantly simplify the synthesis and open up a way to the automated synthesis.

Obviously, solid-phase synthesis can successfully be employed for the preparation of lower oligosaccharides, but in this case its advantages over syntheses in solution are not so apparent. However, on going to higher-molecular-weight oligosaccharides and glycoconjugates the merits of the solid-phase technique will become more conspicuous as in the case of glycoconjugate (*viz.*, glycopeptide and phosphoglycan) synthesis. It is this trend that has become particularly popular in the last few years. And yet major progress was achieved in those syntheses where the elongation of the carbohydrate chain was carried out by enzymic methods, which made it possible to overcome the problem of selective protection of hydroxy groups and its changes in each step of the synthesis.

The feasibility of modification of immobilised monosaccharides presents particular interest and can be illustrated by several examples.

The use of solid-phase techniques in combinatorial chemistry, particularly in a search for carbohydrate structures possessing the optimum biological activity, is one of the most attractive fields. The use of solid-phase synthesis for the preparation of an immense diversity of the so-called 'libraries' of structurally related polyfunctional oligosaccharide structures, excels other methods in many points.

A search for medicinal drugs and other substances possessing specific biological activities among carbohydrate-containing compounds demanded a rapid synthesis of a vast variety of analogues and fragments of biopolymers aimed at a selection of the most active compounds. This in turn required the acquisition of 'libraries' of compounds synthesised by methods of combinatorial chemistry and their further analysis.

It is known that 'combinatorial chemistry' is based on the principle of simultaneous synthesis of a series of related compounds and includes reactions of structurally similar acceptors with donors analogous to each other. This principle can be used

sequentially in different stages of a multistep synthesis.¹⁰¹ The most active compounds are further selected from such 'libraries'.

This strategy attracts considerable attention of specialists in the chemistry of biopolymers who widely utilise the strategy of solid-phase synthesis in the design of peptide and oligonucleotide 'libraries'. Very often, the selection of active components does not require their splitting off the support. The advantages of this approach in a search for biologically active oligosaccharides are especially apparent against the background of their immense structural diversity, which is due to the polyfunctionality of the constituent monosaccharides. The applicability of solid-phase synthesis to the construction of oligosaccharide 'libraries' has been considered.¹⁰² Acquisition of a 'library' comprising ~ 1300 compounds which represent derivatives of β -D-galactopyranosyl-(1-3)-2-deoxy-2-*N*-acylaminogalactopyranoside and include di- and trisaccharides differing in the nature and sequence of monosaccharides, type of intermonomeric glycosidic bonds and substituents at hydroxy and amino groups is a clear example.¹⁰³ A Tentagel-type polymer was used as a support and glycosyl sulphoxides served as glycosyl donors. The resulting 'library' of immobilised oligosaccharides was examined for the specificity of carbohydrate-protein interactions. The most active components were selected using a lectin test.

At present, the principles of combinatorial chemistry including carbohydrate synthesis have become widely used by large manufacturing companies.¹⁰⁴

Special mention should be made in conclusion of a recent review¹⁰⁵ devoted to solid-phase synthesis of oligosaccharides, which suggests that interest in this method continues.

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Quantum-size colloid metal systems

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Abstract. Methods for the preparation of nano-sized metal particles are considered. Theoretical approaches to the analysis of electron behaviour in systems with quantum-size effects are outlined. The results of experimental investigations of the thermodynamic and optical characteristics of small metal particles and thin films are presented. The data of experiments on the electron dynamics in single nanoparticles and nanoparticle ensembles are described. The self-assembly of nanoparticles to form supported ordered structures is considered. The bibliography includes 343 references.

I. Introduction

The interest of researchers in nano-sized systems has markedly enhanced in recent years. Two main lines have taken shape in the research and practical application of systems consisting of elements with sizes from several nanometers to hundred nanometers. The first line includes studies of nano-structured materials. These materials are formed by a large number of nano-sized particles the individual properties of which show themselves in an indirect way — the change in the properties of individual structural units on passing to the nanometer region results in the appearance of new properties of the material. Thus, the ceramics produced from nanometer particles possess enhanced strength, plasticity and wear resistance; alloys of non-compatible metals can be formed; the electrical and magnetic properties of the composites are enhanced, and so on. The achievements concerning imparting new properties to nano-structured materials have been described in the literature fairly comprehensively.^{1,2} Therefore, we do not consider these aspects here.

The second line of research is related to studies of individual nanoparticles. The goals of these studies include both the develop-

ment of methods for the preparation of nanoparticles which would allow one to manipulate them as separate objects and investigation into the physicochemical properties of the nanoparticles synthesised. The history of development of these investigations is fairly long; the results are reflected in monographs.^{3,4}

However, after the publication of these monographs, many new results not reflected yet in review literature have been obtained. The greater part of the experimental data concerning the synthesis and study of the properties of nanoparticles appeared during the last decade. This enhancement of the interest in nanoparticles is due to several reasons

— methods for controlling the size of nanoparticles have been developed;

— new methods for the experimental investigation of nanoparticle structures and electronic and optical characteristics have appeared;

— procedures which enable isolation and stabilisation of individual nanoparticles together with the investigation of their physicochemical properties have been elaborated;

— finally, new properties of nanoparticles were discovered which permit them to be regarded as promising elements of microelectronic devices. The progress attained in the synthesis and study of nanoparticles brought about new problems, which have also stimulated new experimental studies.

In this review, we consider only some of the problems related to the 'quantum-size' colloid metal systems. One should bear in mind the difference between nano-sized (or quantum-size) particles and ultradisperse systems. The latter term has long been used in colloid chemistry. It refers to systems consisting of particles the size of which is smaller than 100 nm; in this case, the contribution of the surface to the thermodynamic characteristics becomes significant, which implies the possibility of changing the surface properties, for example, the surface tension (size corrections). The bulk properties of the particles are usually considered invariant. Meanwhile, the term nano- or quantum-size particles is used to imply colloidal systems of particles, the bulk characteristics of which undergo changes of one type or another caused by particle dimensions. It is this type of systems that is discussed below.

Attention is focused on the preparation of metal nanoparticles in colloidal solutions and on the thermodynamic properties of nanoparticles and metallic films under conditions where quantisation of the electron movement plays a noticeable role. Simulta-

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neously, the main methods used to calculate the electronic structures and thermodynamic characteristics of quantum-size metal systems are outlined. The features of electron dynamics in small metal particles are described and the collective effects in the colloidal ensembles of nanoparticles are considered.

We wittingly restricted consideration to colloidal systems based on metal particles because other nano-sized systems as well as methods for their synthesis and study of properties have already been described in review literature. For example, the results of investigations into the synthesis and encapsulation of nanoparticles in various organic matrices have been reported^{5,6} and various aspects of the physical chemistry of semiconductor nanoparticles have been analysed comprehensively in a review.⁷ In addition, the experimental data concerning nano-sized systems are so numerous that it is impossible to embrace the whole body of information available from the literature in one review.

II. Methods for the synthesis of metal nanoparticles

There exist diverse methods for the preparation of nanoparticles and nanocomposites. In this Section, we shall consider several main methods used to prepare nanoparticles which ensure the possibility of isolating them and separating them from the ensemble. Nanoparticles can present interest as elements of microelectronic devices only when they have been isolated from the ensemble. Therefore, the problem of preparing individual nanoparticles is one of the central problems in today's investigations.

1. Evaporation–condensation method

The evaporation–condensation method has long served as a common method for the preparation of metal nanoparticles.³ According to this method, a metal is evaporated into a flow of an inert gas. Then the flow of the carrier gas with the metal vapour is fed to a chamber, while the temperature of the chamber walls varies according to a previously specified pattern. The pattern of temperature variation is usually calculated taking into account the heat and mass transfer equations and the kinetics of nucleation, in order to attain the necessary rate of condensation of the metal vapour such that the particles have time to grow to the required size before supersaturation is eliminated.

Until recently, the particles thus prepared have been deposited on an inert substrate.^{3,8} The use of a support was necessary in the gas-phase method. Only in this case, were individual particles produced because nano-sized particles are fairly mobile and stick together upon collision; hence, their aggregation has to be suppressed somehow.

Detailed investigations⁹ into the kinetics of aggregation of nanoparticles during their preparation by the evaporation–condensation method have shown that, for example, zinc nanometer particles aggregate over periods of 10–100 ms depending on the conditions of particle growth. They form fractal aggregates with log-normal size distribution, the average size of the aggregates corresponding to the micrometer range.

The evaporation–condensation procedure gives rise to the purest metal particles. This is why it still remains attractive; however, search for the methods that would enable the preparation of nanoparticles without using solid supports is in progress. Methods have been proposed^{10–14} in which the solid support was replaced by frozen argon¹⁰ or by a solvent.^{11,14} According to these (and other similar) techniques, the particles are co-precipitated with the solvent; thus, a composite containing nanoparticles gradually grows. By subsequent heating, the solid composite is converted into a colloidal dispersion of nanoparticles.

Colloidal dispersions obtained in this way are not always stable. In order to obtain stable systems, the methods mentioned above have been modified,^{15,16} namely, surfactants were introduced into the system by co-precipitation (or added subsequently). This gave particles with sizes of up to 1 nm dispersed in

a solvent with a concentration of 10^{20} particles per m^3 . According to the data of electron microscopy, systems prepared in this way contained no particle aggregates.

In early studies,^{15,16} evaporation–condensation experiments were performed with silver particles. This method was studied in more detail in another study in which Ag, Bi, Cu and Te nanoparticles were obtained.¹⁷ It was found that particles with the size from 1 to 10 nm can be obtained in any of the systems tested by varying the pressure and the composition of the carrier gas. The particle size varies as a linear function of pressure. The particles are characterised by a rather narrow size distribution, the corresponding standard deviation being 1.4–1.6.

Particles of Ag/M alloys ($M = \text{Co}, \text{Fe}, \text{Ni}$) with approximately the same characteristics were also prepared by the evaporation–condensation technique.¹⁸

An aerosol method for the preparation of silver nanoparticles coated with a dodecanethiol layer and subsequent introduction of the particles into an organic solvent have been reported.^{19,20} Coating with dodecanethiol was accomplished in the vapour phase immediately after the nucleation of particles by mixing of an aerosol flow with a flow of an inert gas saturated by dodecanethiol vapour. This procedure provided nanoparticles with the best dispersity; however, this was associated with substantial procedural difficulties.

Despite the progress achieved using the evaporation–condensation method, it is mainly employed to produce composite materials and is seldom used to prepare nanoparticles. This is due, first, to the low productivity of the method and, second, to the fact that the size distribution of the resulting particles is too broad, according to the modern criteria. In addition, when using this method, it is difficult to control the size of the nanoparticles formed. As a consequence, standard colloidal methods for the preparation of nanoparticles proved to be more convenient; they have become more attractive owing to the unexpectedly successful use of special surfactants.

2. Reduction from solutions

Chemical reduction is used most widely to synthesise colloidal particles.²¹ Metal salts can be reduced by various reducing agents in the presence of stabilisers (special ligands, polymers, surfactants), which suppress particle aggregation.^{22,23} The reduction yields particles of different sizes. The size cannot be predicted because it is affected simultaneously by several factors: the nature and the concentration of the solvent and the stabilising agent used, reaction temperature, and reaction time. In addition, the particle size is determined to a large extent by the supersaturation developed, higher supersaturation resulting in smaller particles; hence, the size of the particles can be controlled by varying supersaturation.^{21,24}

The degree of supersaturation reached in the experiments is governed by the rate of the chemical reduction, temperature and the amount of the reduced metal spent for the particle formation and growth. The process of particle formation is normally connected with homogeneous (or, perhaps, heterogeneous) nucleation. As a rule, it is limited by the experimental conditions. For this reason, the main way of controlling the particle size is to use growth retardants, which play a dual role. On the one hand, they retard the transfer of the reduced metal from the solution to the particles and thus increase supersaturation. On the other hand, the retardants directly limit the rate of the increase in the particle size. Thus, the choice of the protective shell of the particles appears to be the crucial point in controlling the particle size.

Alkanethiols are known to form dense self-assembled monolayers on the surface of crystalline gold.²⁵ However, until recently, this fact has not been used in the synthesis of nanoparticles. Only in a few publications,^{26,27} were alkanethiols employed in the reduction of gold in a solution of HAuCl_4 by NaBH_4 ; it was found that this process yields virtually monodisperse particles. Originally, so-called two-phase method consisting of two stages has been used for reduction.^{26,27} In the first stage, metal-contain-

ing reagents were transferred from the aqueous phase to the organic phase and then solutions of the surfactant and the reducing agent were added to the organic phase. Subsequently, a single-phase method was developed.^{28–34} According to this method, solutions of the surfactant and the reducing agent were added simultaneously to a metal-containing solution. Presumably, in both cases, gold is reduced to the atomic state, which ends in the nucleation of atoms to give nanocrystals; alkanethiols are adsorbed on the surface of the crystals. The thermodynamics of formation of gold nanoparticles in the presence of alkanethiols has been considered in a study,³⁰ where it was shown that the process of formation of nanoparticles is similar to the process of formation of drops of a water-in-oil microemulsion.

The gold nanocrystals coated by an alkanethiol monolayer, which are formed upon reduction, consist of a metallic core comprising 10 to 5000 atoms and a dense surfactant shell. Almost all the particles exhibit a clear-cut plasmon band in the optical absorption spectrum. The position and the width of the band depend on the particle size and the properties of the adsorbed layer.

The monolayer on nanoparticles is assumed to be self-assembled in the same way as on the surface of bulk samples. The size of nanocrystals depends on the length of the alkyl chain in alkanethiol and on the thiol to gold ratio in the solution.^{27, 32, 35} Examination by electron microscopy shows that gold microcrystals are compact and faceted and have a face-centred cubic (FCC) lattice.³² The crystals are mainly octahedral or icosahedral. The inner area of the microcrystals is pure gold, the sulfur atoms being located on the surface and connected to alkyl chains. These results were obtained from spectroscopy and mass spectrometry.^{32, 36, 37}

Arnold and Reilly³⁷ reported a unique experiment. After the powder of gold nanoparticles coated by alkanethiols had been prepared, it was exposed to powerful laser radiation. As a result, the particles were 'evaporated'. The flow of particles was again irradiated by a laser with the wavelength selected in such a way as to cleave the bond between sulfur and the alkyl chain. This yielded gold nanoparticles with an adsorbed layer of sulfur atoms. The resulting clusters were studied by mass spectrometry. Interpretation of the mass spectra showed that the sulfur atoms form dense monolayers on the surface of gold microcrystals. This result fully confirmed the assumption concerning the formation of dense self-assembled monolayers of alkanethiols on the surface of gold nanoparticles.

A study has been devoted to the dependence of the structure of alkanethiol adlayers coating nanoparticles on the particle size.³⁸ Particles with sizes ranging from 1.2 to 5.2 nm were used in these experiments. The properties of the adlayer were studied by Fourier transform IR spectroscopy, differential scanning calorimetry, wetting and thermal desorption mass spectrometry. The transition from a two-dimensional to three-dimensional packing of alkanethiol molecules was also investigated. It was found that in the case of larger nanoparticles, more ordered conformations of the alkyl chains in the adsorbed alkanethiols are observed. The critical diameter corresponding to the change in the pattern of the adlayer packing was found to be 4.4 nm. For particles with larger diameters, a two-dimensional adlayer is formed, whereas in the case of particles with smaller diameters, elements of a three-dimensional packing show themselves in the adlayer.

In recent years, more complex thiolates have been used for the production of gold nanoparticles,^{39–43} because surfactants with more complicated structures may promote the formation of self-assembled monolayers of nanoparticles (see below). The method is being perfected;⁴⁴ this allows preparation of particles of different metals according to the same procedure.

In particular, alkanethiols have been employed to produce silver nanoparticles^{45–50} (by both single-phase and two-phase procedures). Simultaneous synthesis of gold, silver and platinum nanoparticles has also been accomplished.⁵¹ As for gold, in this case, too, the position of the plasmon band in the optical

absorption spectra depended on the method of preparation and the structure of the environment of metal particles.

3. Reduction in microemulsions

Microemulsions of the 'water-in-oil' type (reverse micelles) have been attracting increasing attention in recent years as micro-reaction media for the preparation of nanoparticles. Microemulsions consist of nano-sized water (or solution) drops dispersed in oil (organic) phase and stabilised by surfactant molecules distributed over the interface. Highly dispersed drops of water are perfect microreactors for the preparation of nanoparticles because the size of drops is a natural restrictor for the dimensions of the growing nanoparticles.

Primarily, microemulsions have been used for the preparation of monodisperse microparticles. The synthesis of Pt, Pd, Rh and Ir particles by the reduction of the corresponding salts in water drops has been described.⁵² Since this publication appeared, microemulsions have been repeatedly used for the preparation of diverse particles of both individual metals and their compounds.

In the 90s, the use of microemulsions to prepare silver,^{53–55} gold,⁵³ platinum, cobalt⁵⁶ and iron⁵⁷ nanoparticles was reported. Nanoparticles were prepared by reduction of the corresponding metal salts by sodium tetrahydroborate or hydrazine. The unique opportunities for controlling the size and shape of nanoparticles from microemulsions have been demonstrated in several studies.^{58–61} The high efficiency of microemulsions in preparing nanoparticles of specified dimensions and shapes was demonstrated most vividly in several studies by Pileni *et al.*^{62–67}. In these works, a functional surfactant, copper bis(2-ethylhexyl)sulfosuccinate Cu(AOT)₂, was used to prepare copper nanoparticles. The surfactant played a dual role — on the one hand, it stabilised drops of water and, on the other hand, it served as a source of copper in the drops.

To prepare nanoparticles, a microemulsion of water drops stabilised by Cu(AOT)₂ and Na(AOT) in isooctane was mixed with a microemulsion of drops of a solution of sodium tetrahydroborate stabilised by Na(AOT). After microemulsions have been mixed, the material exchange between the drops starts and copper is reduced. Due to the presence of natural restrictions, the resulting copper particles are nano-sized.

The size and shape of particles are largely determined by the ratio

$$w = \frac{[\text{H}_2\text{O}]}{[\text{AOT}]}$$

in the microemulsion, because the structure of the microemulsion also depends significantly on this ratio. When $w < 4$, only spherical drops are present, their size being proportional to w . Reduction of copper in such a system gives rise to spherical nanoparticles 1 to 12 nm in diameter; their size is also proportional to w .

Further increase in the content of water ($4 < w < 5.5$) changes the shape of microdrops — they become spheroidal. Correspondingly, reduction in the system affords spherical nanoparticles with diameters of 8.2 and 12 nm and cylindrical particles with a diameter of 12 nm and a length of 18.5 nm. When the relative water content is $5.5 < w < 11$, the microemulsion has a structure of a bi-continuous phase in which nano-spheres with diameters of 6.7 and 9.5 nm and 22.6-nm long nano-rods 9.5 nm in diameter are formed.

When the content of water increases further ($w > 11$), the microemulsion is transformed into a lamellar structure in which only rods with lengths of 300 to 1500 nm and with diameters of 10 to 30 nm are present. According to electron microscopy data, nanoparticles synthesised in microemulsions (including the long rods mentioned above) have defect-free surfaces, which indicates their high quality.

The process of reduction of nanoparticles in microemulsions was studied by numerical modelling by the Monte Carlo method.^{68–70} The modelling data showed that the flexibility of

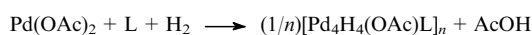
the surfactant monolayer and the surfactant concentration in the system play an important role in the formation of particles in microemulsions. By varying the monolayer flexibility and the content of the surfactant, one can change appreciably the size distribution of nanoparticles and even prepare ensembles with a bimodal size distribution, which is apparently due to the character of evolution of the supersaturation of microemulsions with metal atoms.²⁴

Since surfactants play an important role in the preparation of nanoparticles in microemulsions, the search for new, in particular, non-ionic surfactants which could be used in the synthesis of metal nanoparticles is currently in progress.⁷¹ Syntheses are carried out using non-traditional microemulsions such as water drops in supercritical carbon dioxide.⁷²

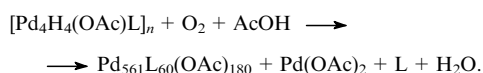
In view of the significant dependence of the size distribution of particles on the character of the exchange of matter between the drops, the use of new methods for the synthesis of nanoparticles in microemulsions which exclude this exchange has started. For example, Revina *et al.*^{73,74} prepared silver nanoparticles by radiation-induced reduction. Studies on the influence of external factors, for example, temperature,^{75,76} on the size and shape of nanoparticles formed in microemulsions have been carried out (in the studies cited, these were gold nanoparticles).

4. Preparation of nanoparticles with a stoichiometric composition

A method yielding metal nanoparticles with a definite composition is most promising as regards investigation of the individual properties of these particles. Primarily, these particles were obtained as metal clusters containing less than ten and, later, more than ten metal atoms (a brief review of the history of preparation of these compounds has been reported⁷⁷). Substantial progress along this line has been achieved by Vargaftik *et al.*,^{78–80} who identified unambiguously palladium clusters containing (in the ideal case) exactly 561 metal atoms. The cluster had the composition $\text{Pd}_{561}\text{L}_{60}(\text{OAc})_{180}$, where L is 1,10-phenanthroline or 2,2'-bipyridine and the OAc groups form the ligand shell. The cluster was produced in a two-stage synthesis^{78–80} including the reduction of $\text{Pd}(\text{OAc})_2$ with hydrogen in an AcOH solution



and subsequent treatment of the high-molecular-weight clusters with oxygen



This cluster belongs to the category of 'magic clusters',[†] *i.e.* those containing strictly definite, 'magic' numbers of metal atoms, namely, 13, 55, 147, 309, 561, ... These numbers correspond to fully occupied atomic layers (shells) of cubooctahedral clusters having a FCC lattice. No clusters with three filled shells have been synthesised up to now;⁸¹ however, clusters with four⁸² ($\text{Pt}_{309}\text{Phen}_5\text{O}_{30}$, Phen is *o*-phenanthroline) and five^{78,83} ($\text{Pd}_{561}\text{Phen}_{36}\text{O}_{200}$) shells have been prepared. The existence of clusters with seven⁸⁴ ($\text{Pd}_{1415}\text{Phen}_{54}\text{O}_{1000}$) and eight⁸⁵ ($\text{Pd}_{2057}\text{Phen}_{38}\text{O}_{1600}$) shells has also been established. The clusters obtained were studied by various methods — high-resolution electron microscopy, EXAFS, Mössbauer spectroscopy, NMR and others. These studies demonstrated that metal atoms actually form a close cubic packing and the distance between the metal atoms virtually coincides with that found for bulk samples. The diameter of the metallic core of the clusters varies from 2.4 to 3.7 nm.

[†] The matter concerns 'magic' numbers in terms of the Mackay–Chini crystal-chemical model. See A L Mackay *Acta Crystallogr.* **15** 225 (1979); P Chini *J. Organomet. Chem.* **200** 37 (1980); B K Teo, N J A Sloan *Inorg. Chem.* **24** 4545 (1985).

The mechanism which provides the synthesis of clusters with a definite number of metal atoms according to the above-described scheme has not been ultimately elucidated. Investigations into the structures of the cluster precursors at different stages of evolution showed that they are shaped like polymeric chains, which are transformed into compact metal particles during heat treatment.⁸⁶ In the case of the cluster with the Pd_{561} core, the metal particle forms a FCC lattice and takes on an icosahedral or twin shape at the final stage.^{87–89}

The methods for the preparation and investigation of clusters with a specified number of atoms are being constantly improved. Modern methods have been employed to perform unique investigations of the thermodynamic and magnetic properties of these nanoparticles. It will be shown below that physical characteristics of 'quantum'-size particles depend essentially on the number of collective electrons they contain.

5. Other methods for the preparation of metal nanoparticles

Among other methods used to synthesise metal nanoparticles, apart from those described above, mention should be made of pulse radiolysis in solutions, which is employed fairly frequently.^{90–97} Under the action of X-ray or ultraviolet radiation or of high-energy electrons, clusters M_2^+ , M_3^+ , ..., M_n^{x+} are formed successively.⁹⁸ Some of these are exceptionally stable. As a result, stable magic clusters are accumulated in the solution. The presence of magic clusters is indicated by the appearance of characteristic bands in the absorption spectra. The contribution of 'non-magic' clusters was found to be insignificant because their lifetimes are fairly short. When using the radiolysis method to prepare nanoparticles, various stabilisers are also added, although in some cases, for example, for aqueous solutions of silver, the use of stabilisers is optional. The nanoparticles formed in the presence of stabilisers are characterised by a higher level of monodispersity and a smaller size. Polymers are used as stabilisers.⁹⁹ The method of radiolysis is also applicable for the preparation of nanoparticles with a mixed composition.^{100,101} This is done either by the reduction of different metal ions present simultaneously in the solution or by preparing first the particles of one metal and coating them subsequently with a shell of a different metal,¹⁰² which is also reduced by radiolysis. By varying radiation doses, one can control the size and the composition of nanoparticles. Apart from the radiation-chemical method, sonochemical preparation of particles is also used.¹⁰³

Metal nanoparticles are often prepared in the presence of polymers.^{104–120} Soluble polymers,^{104–109,118–120} block copolymers^{115,116} or cross-linked matrices are used. The role of the polymeric medium is usually to stabilise the particles. In addition, in the case of solutions of polymers or block copolymers subjected to microphase separation,¹¹⁶ they restrict the particle size. The extent to which the polymer influences the size of nanoparticles depends on the length of the polymer chain¹¹⁹ and on the conditions of synthesis. The synthesis can require a fairly sophisticated procedure; for example, nanoparticles have been prepared using supercritical carbon dioxide.¹¹¹ In another study,¹²⁰ polymers were used to ensure high yields of nanoparticles of noble metals. One more problem was solved simultaneously, namely, transfer of the nanoparticles into a colloidal solution of any concentration, replacement of the solvent being possible.

Various templates are used in the synthesis of nanoparticles in order to impart a specified shape to them and to restrict their size. The materials used for this purpose included polymeric membranes^{121,122} (this permitted the researchers to grow cylindrical particles), high-porosity oxide films¹²³ and specially prepared substrates,^{124–126} which often provided the possibility of preparing catalysts ready for use or ordered structures constructed from nanoparticles. In some cases, nanoparticles and composites based on them are prepared using the 'sol-gel' technology,^{127–132} or by growing particles in biological^{133,134} and liquid-crystalline¹³⁵ systems. A method for the preparation of nanoparticles under electric discharge in solution has been proposed.¹³⁶

III. Methods for calculation of the electronic properties of metal nanoparticles

1. The density functional method

The *ab initio* Hartree–Fock method has found wide use in the calculation of properties of many-electron systems. In this method, the properties of a many-particle system are determined by calculating the orbitals of separate electrons moving in the self-consistent field of other electrons and atomic nuclei. The Hartree–Fock method allows one to find the wave functions of electrons without invoking adjustable parameters. The main obstacle to the use of this method is the complexity of calculations; the time it takes to perform calculations increases as N^4 , where N is the number of electrons in the system. For this reason, the Hartree–Fock method is mainly used to perform calculations for atoms or relatively small molecules and clusters.

The greatest progress in calculations for many-electron systems has been attained in the last decades using the density functional method. The time needed for calculations by this method increases with an increase in the number of electrons much more slowly; at present, this method is widely used for calculations for various systems with a large number of electrons including polyatomic molecules, complexes, clusters, and condensed media.

There are two approaches in the density functional method, namely, integral and local approaches. The former dates from an original study by Hohenberg and Kohn,¹³⁷ while the latter is a modification of the theory proposed by Kohn and Sham.¹³⁸ We shall consider these approaches in relation to a system of N non-relativistic electrons described by a Hamiltonian

$$H = T + V + U. \quad (1)$$

Here T is the operator for the kinetic energy of electrons

$$T = -\frac{1}{2m} \hbar^2 \sum_i \Delta_i, \quad (2)$$

m is the mass of an electron, Δ_i is the Laplacian for an i th particle, V is the potential energy operator for a system of electrons in an external field and U is the operator of the electrostatic repulsion energy of electrons.

It was shown¹³⁷ that the electron density distribution $\rho(\mathbf{r})$ determines unambiguously all the main properties of a many-electron system including the wave function. The energy of a many-electron system in an external field $v(\mathbf{r})$ is a functional of $\rho(\mathbf{r})$

$$E[\rho(\mathbf{r})] \equiv \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + G[\rho(\mathbf{r})]. \quad (3)$$

The last term depends on the wave function Ψ of the system of electrons, determined by the distribution of their density

$$G[\rho(\mathbf{r})] = \int \Psi^*[\rho(\mathbf{r})](T + U)\Psi[\rho(\mathbf{r})]d\mathbf{r} \quad (4)$$

(the character * means the complex conjugate).

The minimum energy corresponds to the ground state of the system

$$E[\rho(\mathbf{r})] \geq E[\rho_g(\mathbf{r})], \quad (5)$$

where $\rho_g(\mathbf{r})$ is the electron density distribution in the ground state.

However, the fundamentality and simplicity of the Hohenberg and Kohn theorem¹³⁷ are fraught with latent difficulties. Determination of the electronic density and other characteristics of an electron system requires that the explicit form of functional (3) be known. However, the explicit form of this functional is unknown; thus, additional statements are needed to find the form of $E[\rho(\mathbf{r})]$. Functional (3) can formally be represented as follows:

$$E[\rho(\mathbf{r})] = \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + T_0[\rho(\mathbf{r})] + \frac{1}{2} \int \frac{e^2 \rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho(\mathbf{r})], \quad (6)$$

where e is the charge of an electron, $\mathbf{r}, \mathbf{r}'$ are space coordinates.

The second term is the kinetic energy of non-interacting electrons T_0 , and the third term is the energy of electrostatic interaction between them.

The last term, $E_{xc}[\rho(\mathbf{r})]$, is an electron density functional depending implicitly on $v(\mathbf{r})$. It is usually called exchange correlation energy of electron gas. Actually, equality (6) is the definition of this functional. Thus, a fundamental problem faced by the density functional method is to elucidate the form of the functional $E_{xc}[\rho(\mathbf{r})]$. There are several approximate methods for the calculation of this functional.¹³⁹

Minimisation of functional (3) in a one-electron approximation results in a set of self-consistent equations (Kohn–Sham equations)

$$\left(-\frac{1}{2} \frac{\hbar^2}{m} \Delta_j + v(\mathbf{r}) + \int \frac{e^2 \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}) - E_j \right) \phi_j(\mathbf{r}) = 0. \quad (7)$$

Here, $\rho(\mathbf{r})$ is the electron density

$$\rho(\mathbf{r}) = \sum_{j=1}^N \phi_j^*(\mathbf{r})\phi_j(\mathbf{r}), \quad (8)$$

$v_{xc}(\mathbf{r})$ is the exchange correlation potential

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})}, \quad (9)$$

E_j are single-electron energy levels, $\phi_j(\mathbf{r})$ are single-electron wave functions, $j = 1, \dots, N$.

The ground-state energy for a many-electron system is given in this approximation by the relation

$$E = \sum_{j=1}^N E_j - \frac{1}{2} \int \frac{e^2 \rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' - \int v_{xc}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r}. \quad (10)$$

Formally, the Kohn–Sham equations are exact; however, there exists the problem of the relationship between $v_{xc}(\mathbf{r})$ and electron density. At present, it can be regarded proven that the potential $v_{xc}(\mathbf{r})$ can be determined unambiguously; in this case, the use of single-electron approximation does not play a crucial role.^{140–142} It has also been proven that, by using the potential $v_{xc}(\mathbf{r})$, one can reproduce precisely the distribution of electron density in the system¹⁴³ and that the upper occupied level of an isolated system of electrons in the absence of an external field is related uniquely to the ionisation potential;¹⁴⁴ in addition, the asymptotic variation of the electron density for a system with a finite number of electrons is entirely determined by the upper occupied single-electron function (orbital).

As has already been noted, the use of the density functional method requires at least an approximate way of finding $E_{xc}[\rho(\mathbf{r})]$. For a uniform electron gas, it can formally be written in the local density approximation that

$$E_{xc} = \int \rho \epsilon_{xc} d\mathbf{r}, \quad (11)$$

where ϵ_{xc} is the local exchange correlation energy of electrons, equal to $-9[(3/4\pi)\rho]^{1/3}$. For non-uniform systems, the local energies ϵ_{xc} were found as the gradient expansion^{145–149}

$$\epsilon_{xc} = g[\rho(\mathbf{r}), \nabla \rho(\mathbf{r}), \nabla^2 \rho(\mathbf{r})]. \quad (12)$$

Other attempts to determine the exchange correlation energy as the electron density functional have also been undertaken.^{150, 151} In particular, it has been represented as a non-local functional.¹⁵²

2. The method of statistical functions

In the investigations of many-electron systems including nanoparticles, considered in this review, the method of statistical distribution functions is also used. This method has been used successfully to study the surface properties of various quantum objects^{153–156} and the structures of clusters;¹⁵⁷ it can also be used to investigate the dynamic processes in quantum systems.¹⁵⁶ For this reason, we shall outline briefly the main principles of the distribution functions method.

In quantum mechanics, the role of distribution functions is played by the density matrix¹⁵⁸ for N particles, $\rho_N(t)$ (t is time). In the coordinate representation, the density matrix of a system is a function of coordinates and spin variables of all particles

$$\langle \sigma', R' | \rho_N(t) | \sigma, R \rangle = \sum_i P_i \Psi_i^*(R', \sigma') \Psi_i(R, \sigma), \quad (13)$$

where R and σ are sets of coordinates $R = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ and spin variables $\sigma = (\sigma_1, \dots, \sigma_N)$, and P_i is the probability that the system occurs in a pure state i with the wave function Ψ_i . By means of the density matrix, the average value of any operator $\hat{T}$ can be written in the form

$$\langle \hat{T} \rangle = \sum_{\sigma} \int dR \hat{T} \langle \sigma', R' | \rho_N | \sigma, R \rangle \Big|_{\substack{\sigma'=\sigma, \\ R'=R}}, \quad (14)$$

the operator $\hat{T}$ acting on the ‘non-primed’ variables of the density matrix. After the action of the operator, the primed and non-primed variables are taken to be equal.

The diagonal elements of the density matrix $\langle \sigma, R | \rho_N | \sigma, R \rangle$ determine the probabilities of distribution of the system over coordinates and spin states of the particles.

The density matrix satisfies the Liouville quantum equation

$$\left(i\hbar \frac{\partial}{\partial t} - \hat{H} + \hat{H}'^* \right) \langle \sigma', R' | \rho_N | \sigma, R \rangle = 0. \quad (15)$$

Here $\hat{H}$ is the Hamiltonian for a system of particles acting on the non-primed variables, while $\hat{H}'^*$ acts on primed variables.

For a system of particles with pair interaction, in the absence of an external field, the Hamiltonian has the form

$$\hat{H} = \sum_i \left(-\frac{\hbar^2}{2m} \Delta_i \right) + \sum_{1 \leq i < j \leq N} u(\mathbf{r}_i - \mathbf{r}_j),$$

where Δ_i is the Laplacian operating on the coordinates of an i th particle and $u(\mathbf{r}_i - \mathbf{r}_j)$ is the energy of pair interaction of particles.

Wigner¹⁵⁹ introduced a special (mixed) representation for a density matrix in which the distributions of particles over coordinates $R = (\mathbf{r}_1, \dots, \mathbf{r}_N)$ and momenta $P = (\mathbf{p}_1, \dots, \mathbf{p}_N)$ appear. The density matrices in the Wigner representation and those in the coordinate representation are related as

$$F(R, P, t) = \frac{1}{(2\pi)^{3N}} \int d\tau [\exp(-i\tau P)] \times \langle \sigma, R - \frac{\hbar}{2}\tau | \rho_N(t) | \sigma, R + \frac{\hbar}{2}\tau \rangle, \quad (16)$$

where $\tau = (\tau_1, \dots, \tau_N)$, $R - \frac{\hbar}{2}\tau = (\mathbf{r}_1 - \frac{\hbar}{2}\tau_1, \dots, \mathbf{r}_N - \frac{\hbar}{2}\tau_N)$ and $\tau P = (\tau_1 \mathbf{p}_1 + \dots + \tau_N \mathbf{p}_N)$.

In the general case, the mixed representation $F(R, P, t)$ can be used to derive separate distributions over coordinates and over particle momenta

$$F_R(R, t) = \int F(R, P, t) dP, \quad (17)$$

$$F_P(P, t) = \int F(R, P, t) dR.$$

Using the Wigner density matrix, the average value of any operator $\hat{T}(R, P)$ depending on R and P is calculated from the formula

$$\langle \hat{T} \rangle = \int dR dP \hat{T}(R, P) F(R, P). \quad (18)$$

Thus, the mixed representation for the density matrix (16) is similar to the ordinary distribution function used in classical statistical mechanics; its standard expressions can be employed to find the average values of physical quantities. There is, however, one fundamental difference between the classical and quantum descriptions: unlike the classical distribution function of particles over coordinates and momenta, the density matrix $F(R, P, t)$ can acquire not only positive but also negative values. This is due to the fact that the function $F(R, P, t)$ has no clear physical meaning because it is known that particle coordinates and momenta cannot be measured simultaneously in quantum mechanics. Only the distribution functions $F_R(R, t)$ and $F_P(P, t)$ have a physical meaning; they are positive.

The Liouville quantum equation (15) in the mixed representation has the form

$$\begin{aligned} & \left(\frac{\partial}{\partial t} + \sum_{i=1}^N \frac{\mathbf{p}_i}{m} \frac{\partial}{\partial \mathbf{r}_i} \right) F_{\sigma', \sigma}(P, R) = \\ & = \frac{1}{i\hbar} \int \frac{d\tau}{(2\pi)^3} \sum_{i \neq j} \int d\mathbf{p}'_i d\mathbf{p}'_j \delta(\mathbf{p}'_i + \mathbf{p}'_j - \mathbf{p}_i - \mathbf{p}_j) \times \\ & \times \exp \left\{ \frac{1}{2} i\tau [(\mathbf{p}'_i - \mathbf{p}'_j) - (\mathbf{p}_i - \mathbf{p}_j)] \right\} \left[u \left(\left| \mathbf{r}_i - \mathbf{r}_j + \frac{1}{2} \tau \hbar \right| \right) - \right. \\ & \left. - u \left(\left| \mathbf{r}_i - \mathbf{r}_j - \frac{1}{2} \tau \hbar \right| \right) \right] \times \\ & \times F_{\sigma', \sigma}(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_{i-1}, \mathbf{p}'_i, \mathbf{p}_{i+1}, \dots, \mathbf{p}_{j-1}, \mathbf{p}'_j, \mathbf{p}_{j+1}, \dots, \mathbf{p}_N, t). \end{aligned} \quad (19)$$

The N -particle equation (19) can be transformed by standard quantum-mechanics methods¹⁶⁰ into a sequence of engaged equations for one-, two- and many-particle distribution functions. Thus, for one-particle distribution function, after integration over coordinates and spin variables of particles 2, 3, ..., N , we have

$$\begin{aligned} & \left(\frac{\partial}{\partial t} + \frac{\mathbf{p}_1}{m} \frac{\partial}{\partial \mathbf{r}_1} \right) F_{\sigma'_1, \sigma_1}(\mathbf{r}_1, \mathbf{p}_1, t) = \frac{1}{i\hbar} \frac{1}{(2\pi)^3} \left(\frac{N}{V} \right) \times \\ & \times \int d\tau d\mathbf{r}_2 d\mathbf{p}'_2 d\mathbf{p}'_1 \sum_{\sigma_2} \exp[i\tau(\mathbf{p}'_1 - \mathbf{p}_1)] \times \\ & \times \left[u \left(\left| \mathbf{r}_1 - \mathbf{r}_2 + \frac{1}{2} \tau \hbar \right| \right) - u \left(\left| \mathbf{r}_1 - \mathbf{r}_2 - \frac{1}{2} \tau \hbar \right| \right) \right] \times \\ & \times F_{2\sigma'_1, \sigma'_2, \sigma_1, \sigma_2}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t). \end{aligned} \quad (20)$$

The equation for a two-particle function $F_{2\sigma'_1, \sigma'_2, \sigma_1, \sigma_2}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t)$ is more cumbersome.

The possibility of solving Eqn (20) is related to the choice of an appropriate approximation for the two-particle distribution function. Here we consider the simple self-consistent field approximation in which the two-particle function F_2 is represented as a product of one-particle functions

$$F_{2\sigma'_1, \sigma'_2, \sigma_1, \sigma_2}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2, t) = F_{1\sigma'_1, \sigma_1}(\mathbf{r}_1, \mathbf{p}_1, t) F_{1\sigma'_2, \sigma_2}(\mathbf{r}_2, \mathbf{p}_2, t). \quad (21)$$

Let us introduce a density matrix normalised to the density of the number of particles

$$f_{\sigma', \sigma}(\mathbf{r}, \mathbf{p}, t) = \frac{N}{V} F_{1\sigma', \sigma_1}(\mathbf{r}_1, \mathbf{p}_1, t). \quad (22)$$

Then, in the self-consistent approximation, Eqn (20) for a steady-state case acquires a simple form¹⁵³ (the summation is done over spin variables)

$$\frac{\mathbf{p}}{m} \frac{\partial f(\mathbf{r}, \mathbf{p})}{\partial \mathbf{r}} = \frac{1}{i\hbar} \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} d\tau \int_{-\infty}^{\infty} d\boldsymbol{\eta} [\exp i\tau(\boldsymbol{\eta} - \mathbf{p})] f(\mathbf{r}, \tau) \times \quad (23)$$

$$\times \left[u_{\text{ef}}\left(\mathbf{r} + \frac{1}{2}\tau\hbar\right) - u_{\text{ef}}\left(\mathbf{r} - \frac{1}{2}\tau\hbar\right) \right],$$

where $u_{\text{ef}}(\mathbf{r})$ is the effective self-consistent potential energy

$$u_{\text{ef}}(\mathbf{r}) = u_e(\mathbf{r}) + \int v_{\text{el}}(\mathbf{r} - \mathbf{r}') f(\mathbf{r}', \mathbf{p}') d\mathbf{r}' d\mathbf{p}', \quad (24)$$

u_e is the external potential acting on particles (electrons) and v_{el} is the energy of electron–electron interaction.

Now we consider the metal–vacuum interface. Let us assume that axis z is normal to the metal surface, which coincides with the plane $z = 0$ and that the electron–electron interaction is purely electrostatic (without allowance for exchange and correlation). In this case, the effective potential u_{ef} is determined by the self-consistent Poisson equation the solution of which in the unidimensional variant has the form

$$u_{\text{ef}}(z) = 4\pi e^2 \int_{-\infty}^z d\xi q(\xi) \int_{-\infty}^{\xi} d\zeta q(\zeta), \quad (25)$$

where the electron density $\rho(z)$, appearing in the expression for the charge density

$$q(z) = n_+(z) - \rho(z) \quad (26)$$

is determined from the solutions of Eqn (23), while the density of ions $n_+(z)$ is considered specified. As usual, we shall assume that the density $\rho(z)$ is related to the function $f(z, \mathbf{p})$ by the equation

$$\rho(z) = \int f(z, \mathbf{p}) d\mathbf{p}. \quad (27)$$

Since the effective potential acting on electrons does not depend on the coordinates x and y , then

$$u_{\text{ef}}\left(\mathbf{r} + \frac{1}{4}\tau\hbar\right) = u_{\text{ef}}\left(z + \frac{1}{4}\tau\hbar\right),$$

where $\tau = \tau_z$. The function $f(\mathbf{r}, \mathbf{p})$ does not depend on the coordinates x or y either. Therefore, the left-hand and the right-hand parts of equality (23) can be integrated over the variables $\eta_x, \eta_y, \tau_x, \tau_y, p_x$ and p_y . After integration, we have

$$\frac{p}{m} \frac{\partial f(z, \mathbf{p})}{\partial z} = \frac{1}{2\pi i \hbar} \int_{-\infty}^{\infty} d\tau d\eta [\exp i\tau(\boldsymbol{\eta} - \mathbf{p})] f(z, \eta) \times \quad (28)$$

$$\times \int_{z-\frac{1}{2}\tau\hbar}^{z+\frac{1}{2}\tau\hbar} dy \int_{-\infty}^y q(x) dx.$$

Here, $\tau = \tau_z, \eta = \eta_z$ and $p = p_z$.

Solution of Eqn (28) can be found by standard methods of the kinetic theory, for example, by using the well-developed method of moments. Roldughin and Martynov have shown¹⁵³ how an equation for the electron density near the surface can be derived from Eqn (28). A number of asymptotic dependences can be derived in this way. For example, for the density of electrons in a metal far from the surface, Friedel oscillations were found

$$\rho(z) = n_+ + A \frac{\sin[2p_F(z + z_0)/\hbar]}{(2p_F z/\hbar)^2}, \quad (29)$$

where A is a coefficient, p_F is the Fermi momentum. In a vacuum at $z \rightarrow \infty$, we have

$$\rho(z) = B \exp\left(-\frac{z}{R_s}\right), \quad (30)$$

where B is a coefficient, R_s is a typical length of the attenuation of the electron density near the surface.

Comparison of the results obtained by the method of quantum distribution functions with the results of calculations by the density functional method in the same approximation shows¹⁵³ that the method of quantum distribution functions provides more precise and detailed information on the electron density distribution in metals. In particular, it describes the Friedel oscillations and predicts a steeper decay of the electron density near the metal surface where the simple exponential variation of the charge density vs. distance to the surface is established only asymptotically, which has a clear physical meaning.

3. Phenomenological method

Many properties of electronic systems the thermodynamic characteristics of which are substantially influenced by the surface can be determined using a simpler method which we would conventionally call the phenomenological method. This technique was used to calculate the disjoining pressure (see below) in thin films of liquid metals¹⁶¹ and to determine the chemical potential of electrons in small particles.¹⁶² An interesting feature of this method is the fact that the shift of the chemical potential of electrons is determined, as a first approximation, only by the surface to volume ratio for the object. The geometrical shape of the system and the contribution of the quantisation of energy levels manifest themselves in higher approximations.¹⁶¹

The method is based on the relationship between the density of electronic states $\rho(E)$ (E is the energy of electrons) and the Green function $G(\mathbf{r}, \mathbf{r}', E)$ ¹⁶³

$$\rho(E) = \frac{1}{\pi} \text{Im} \int G(\mathbf{r}, \mathbf{r}', E)_{\mathbf{r} = \mathbf{r}'} d\mathbf{r}. \quad (31)$$

Electrons are considered to move in some self-consistent field. The presence of this field is taken into account by introduction of effective boundary conditions for the electron wave function or the Green function

$$\frac{\partial G(\mathbf{r}_s, \mathbf{r}')}{\partial n} - \lambda_s G(\mathbf{r}_s, \mathbf{r}') = 0. \quad (32)$$

where $\mathbf{r}_s$ is a vector belonging to the particle (or film) surface, $\mathbf{n}$ is an internal normal to the surface, λ_s a parameter of the theory which can be interpreted as the reciprocal of the thickness of the electron cloud near the metal surface. In order to find the parameter λ_s , one has to solve the problem of electron density distribution near the particle or film surface by one of the methods described above.

The Green function can be found from the equation¹⁶⁴

$$\Delta G(\mathbf{r}, \mathbf{r}', E) + k^2 G(\mathbf{r}, \mathbf{r}', E) = -\delta(\mathbf{r} - \mathbf{r}'), \quad (33)$$

where

$$k = \sqrt{\frac{2m}{\hbar^2} (E + i\gamma)},$$

γ is the width of the energy levels of electrons, which can be related to lattice vibrations and other factors, $\delta(\mathbf{r} - \mathbf{r}')$ is a delta function.

A method for finding the Green function $G(\mathbf{r}, \mathbf{r}', E)$ and the density of states $\rho(E)$ has been proposed by Balian and Bloch,¹⁶⁴ who found them as an expansion in terms of ‘multiple scattering’ of electrons by the surface. The Green function was represented as the sum

$$G(\mathbf{r}, \mathbf{r}', E) = G_0(\mathbf{r}, \mathbf{r}', E) + G_1(\mathbf{r}, \mathbf{r}', E). \quad (34)$$

Here $G_0(\mathbf{r}, \mathbf{r}', E) = [\exp(ik|\mathbf{r} - \mathbf{r}'|)]/4\pi|\mathbf{r} - \mathbf{r}'|$ is the Green function for free electron gas and $G_1(\mathbf{r}, \mathbf{r}', E)$ is a correction to this function; it was proposed to determine the correction as the potential of a simple layer

$$G_1(\mathbf{r}, \mathbf{r}', E) = \int_S dS_\alpha G_0(\mathbf{r}, \mathbf{a}, E) \mu_1(\mathbf{a}, \mathbf{r}'). \quad (35)$$

The parameter $\mathbf{a}$ used here and $\boldsymbol{\beta}, \boldsymbol{\gamma}$, and $\boldsymbol{\delta}$ used in the subsequent formulae are the coordinates of points in the layer and $\mu_1(\mathbf{a}, \mathbf{r}')$ is a

function characterising this layer. The derivative of the potential of the simple layer along the normal to the surface satisfies the equation

$$\frac{\partial G_1^{(+)}(\mathbf{b}, \mathbf{r}')}{\partial n_\beta} - \frac{\partial G_1^{(0)}(\mathbf{b}, \mathbf{r}')}{\partial n_\beta} = -\frac{1}{2}\mu_1(\mathbf{b}, \mathbf{r}'), \quad (36)$$

where the subscripts (+) and (0) at the Green function mean that these derivatives are calculated when $\mathbf{r}$ approaches the surface from the inside and directly on the surface (for $\mathbf{r} = \mathbf{b}$), respectively.

From Eqns (32), (34)–(36), one can derive integral equation for $\mu_1(\mathbf{a}, \mathbf{r}')$

$$\begin{aligned} \mu_1(\mathbf{b}, \mathbf{r}') + 2 \int_S \lambda_s dS_x G_0(\mathbf{b}, \mathbf{a}) \mu_1(\mathbf{a}, \mathbf{r}') = 2 \left(\frac{\partial}{\partial n_\beta} - \lambda_s \right) G_0(\mathbf{b}, \mathbf{r}') + \\ + 2 \int_S dS_x \frac{\partial G_0(\mathbf{b}, \mathbf{a})}{\partial n_\beta} \mu_1(\mathbf{a}, \mathbf{r}'). \end{aligned} \quad (37)$$

This equation can be solved rather simply.¹⁶⁴ The Green surface function $\Gamma(\mathbf{a}, \mathbf{b})$ is introduced; it is defined as the solution of the integral equation

$$\Gamma(\mathbf{b}, \gamma) + 2 \int_S \lambda_s dS_x G_0(\mathbf{b}, \mathbf{a}) \Gamma(\mathbf{a}, \gamma) = \delta(\mathbf{b} - \gamma). \quad (38)$$

By multiplying Eqn (37) by $\Gamma(\mathbf{b}, \gamma)$ and integrating over S_β , we obtain an equation for $\mu_1(\mathbf{a}, \mathbf{r}')$ having the following form:

$$\begin{aligned} \mu_1(\mathbf{b}, \mathbf{r}') = 2 \int_S dS_\beta \left(\frac{\partial}{\partial n_\beta} - \lambda_s \right) G_0(\mathbf{b}, \mathbf{r}') + \\ + 2 \int_S dS_\beta \int_S dS_\gamma \Gamma(\mathbf{a}, \mathbf{b}) \frac{\partial G_0(\mathbf{b}, \gamma)}{\partial n_\beta} \mu_1(\gamma, \mathbf{r}'). \end{aligned} \quad (39)$$

This equation is solved by the iteration method; for relatively smooth surfaces, the iterative process rapidly converges.¹⁶⁴ This gives the series

$$\begin{aligned} \mu_1(\mathbf{b}, \mathbf{r}') = 2 \int_S dS_\beta \left(\frac{\partial}{\partial n_\beta} - \lambda_s \right) G_0(\mathbf{b}, \mathbf{r}') + \\ + 4 \int_S dS_\delta \int_S dS_\beta \int_S dS_\gamma \Gamma(\mathbf{a}, \mathbf{b}) \frac{\partial G_0(\mathbf{b}, \gamma)}{\partial n_\delta} \Gamma(\gamma, \mathbf{b}) \left(\frac{\partial}{\partial n_\beta} - \lambda_s \right) G_0(\mathbf{b}, \mathbf{r}') + \dots, \end{aligned} \quad (40)$$

when the λ_s value is constant, the Fourier transform (p -variable) of the function $\Gamma(\mathbf{a}, \mathbf{b})$ can be readily found

$$\hat{\Gamma}(p) = \frac{\sqrt{p^2 - k^2}}{\lambda_s + \sqrt{p^2 - k^2}}, \quad (41)$$

which allows the calculation of every term of the series in expansion (40).

After the Green function $G(\mathbf{r}, \mathbf{r}', E)$ and the density of state $\rho(E)$ have been found, one can determine all thermodynamic characteristics of electrons in small particles and films.

4. Statistics of the electron energy levels in small particles

Yet another method suitable for determination of characteristics of the electrons in small particles is based on analysis of distribution of energy levels. A nanoparticle is never shaped like an ideal sphere. All methods used to prepare nanoparticles imply the presence of impurities on the surface. The distribution of impurities over the particle surface is not ideal either. As a result, it is impossible to calculate the energy levels with an inaccuracy substantially smaller than the distance between the levels. Kubo was the first to notice this.¹⁶⁵ He proposed that the energy levels be regarded as being randomly distributed; the average distance between them was specified to be

$$\Delta_\mu \approx \frac{E_F}{N},$$

where E_F is the energy of Fermi electrons in the particle and N is the number of electrons. The Kubo assumption is matched by the Poisson probability density for the distance Δ between the neighbouring levels

$$P(\Delta) = \frac{1}{\Delta_m} \exp\left(-\frac{\Delta}{\Delta_m}\right). \quad (42)$$

Kubo used this probability density to calculate the heat capacity and the magnetic susceptibility of small particles.

Later, Gor'kov and Elyashberg¹⁶⁶ pointed out that Kubo's results were erroneous. This conclusion was based on the results obtained by Wigner,^{167, 168} who considered the statistics of nuclear energy levels and showed the presence of correlations between them. Wigner's results have been mathematically substantiated and the character of correlations between energy levels has been established.^{169–171}

It was shown^{169, 170} that, in terms of the type of transformations that leave the Hamiltonian for a system of particles invariant, three ensembles can be distinguished, each being characterised by its own statistics of the distribution of levels: (i) orthogonal ensemble — for a system with an integer spin invariant with respect to the inversions of time and space coordinates; (ii) symplectic ensemble — for random interactions of particles invariant with respect to time inversion and for a half-integral spin of the system; (iii) unitary ensemble — for systems not invariant with respect to time inversion.

The orthogonal ensemble appears in the presence of a weak external magnetic field, either weak or strong spin-orbital interaction and with an even number of electrons in the particle. The symplectic ensemble implies strong spin-orbital interaction, able to mix the levels corresponding to different spins of the system; the number of electrons in the system should be odd. The unitary ensemble describes systems occurring in a strong magnetic field.

The normalised distribution of N ordered energy levels for any of the three ensembles is determined from the equation¹⁷²

$$W_\beta(E_1, E_2, \dots, E_N) = C_\beta \exp\left(-\frac{\beta}{2} \sum_i E_i^2\right) \prod_{j < k} |E_j - E_k|^\beta, \quad (43)$$

where C_β is a normalisation factor,

$$\int \dots \int W_\beta dE_1 \dots dE_N = 1, \quad (44)$$

and the parameter $\beta = 1, 2$ and 4 for the orthogonal, unitary and symplectic ensembles, respectively.

The physical properties of small particles depend on the distribution of the electronic energy levels located directly near the Fermi level. The distribution of these levels is found for the limit $N \rightarrow \infty$ by integration over a large number of levels (except for those located in the central region of the energy spectrum)

$$P_\beta(E_i \dots E_{i+n}) = \quad (45)$$

$$= \lim_{N \rightarrow \infty} \int \dots \int W_\beta(E_1 \dots E_N) dE_1 \dots dE_{i-1} dE_{i+n+1} \dots dE_N.$$

In the central part of the spectrum, the absolute position of the level does not play any role, only the distribution of the gaps between the levels being significant

$$\Delta_1 = E_{i+1} - E_i, \Delta_2 = E_{i+2} - E_{i+1} \dots \Delta_n = E_{i+n} - E_{i+n-1}. \quad (46)$$

The role of the distributions¹⁷³ $P_0(\Delta)$, $P_1(\Delta_1, \Delta_2)$, $P_2(\Delta_1, \Delta_2, \Delta_3)$, ... successively decreases because the use of higher approximations in the calculation of thermodynamic properties results only in the refinement of calculations done in the first approximation. Below we restrict our consideration to the first approximation. In this case, the densities of distribution of the levels in the three above-mentioned ensembles at small Δ are given by the expressions

$$\begin{aligned}
P_{\text{ort}}(\Delta) &= \frac{1}{2} \pi \frac{\Delta}{\Delta_m} \exp \left[-\frac{1}{4} \pi \left(\frac{\Delta}{\Delta_m} \right)^2 \right], \\
P_{\text{sym}}(\Delta) &= \left(\frac{8}{3\sqrt{\pi}} \right)^6 \left(\frac{\Delta}{\Delta_m} \right)^4 \exp \left[-\frac{69}{9\pi} \left(\frac{\Delta}{\Delta_m} \right)^2 \right], \\
P_{\text{un}}(\Delta) &= \frac{32}{\pi^2} \left(\frac{\Delta}{\Delta_m} \right)^4 \exp \left[-\frac{4}{\pi} \left(\frac{\Delta}{\Delta_m} \right)^2 \right].
\end{aligned} \quad (47)$$

The corresponding curves are shown in Fig. 1, which also presents the density of probabilities for the Poisson law. It can be seen that real distribution laws substantially differ from the Poisson law; the difference is that the density of distribution of levels for real systems tends to zero when $\Delta \rightarrow 0$. This means that the probability of finding closely located levels in small particles is exceptionally low; it is said that levels ‘repel’ one another. The repulsion of energy levels changes crucially the thermodynamic properties of small particles at low temperatures.

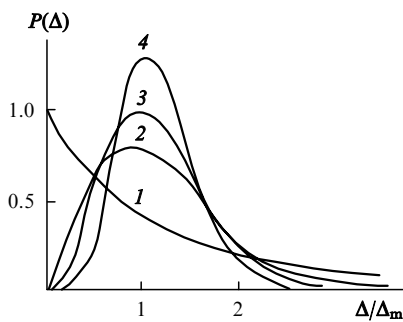


Figure 1. Probability densities for distances between the levels in the Poisson (1), orthogonal (2), unitary (3) and symplectic (4) ensembles.

IV. The electronic and thermodynamic properties of small metal particles and thin films

1. The electronic structure of small particles

As noted above, the density functional method is used most often to calculate the electronic structures of clusters and small particles (see reviews^{174–176}). Even for clusters consisting of several atoms (and even in the absence of ligand shells), various approximations are used. The best known approximation is the jellium model, according to which a cluster is represented as consisting of two subsystems, namely, the positive charge distributed uniformly over the bulk, which models the ion core of the cluster, and delocalised electrons.

Calculations carried out within the framework of this model provide an explanation for the shell character of the electronic structure of atomic clusters of univalent metals. For ‘bare’ spherical clusters, single-electron energy levels correspond to the model of a spherically symmetrical potential well and form the sequence of states $1s, 1p, 1d, 2s, 1f, 2p$, etc. Owing to the spherical symmetry, the energy states of electrons are degenerate, the degeneracy order being equal to $2(2l + 1)$ (with allowance for the electron spin). The numbers of electrons needed for the full occupancy of the shell can be easily found. They are 2, 8, 18, 20, 34, 40, etc. This sequence of filling the shells is matched by local extrema of the ionisation potentials of univalent metal clusters¹⁷⁵ (Fig. 2), although the jellium model does not reproduce the dependence of the ionisation potential of a cluster on its dimensions for a spherically symmetrical core. The mass spectrum of the most stable clusters corresponding to the so-called magic numbers cannot be reproduced in this model either. Note that clusters with closed electron shells, as shown by Brack,¹⁷⁶ are spherically symmetrical. The inadequacy of the spherical model for clusters with open shells is due to the deviation of the shape of these clusters from spherical. Calculations have been carried out^{177, 178}

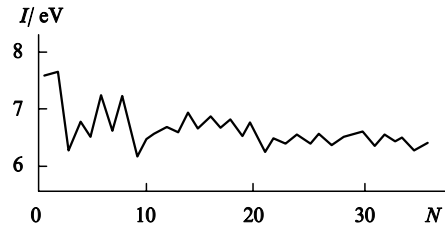


Figure 2. Ionisation potential (I) vs. the number (N) of atoms in the silver cluster.¹⁷⁵

in which the distortion of the central field acting on the electrons was taken into account in the jellium model for clusters with partially occupied electron shells by replacing the spherical shape of the cluster by a spheroidal shape. The calculated characteristics of clusters, for example, of sodium clusters, such as the total energy, polarisability and ionisation potential follow a more complex dependence on the system dimensions than those in the spherical model and agree better with the experimental data.

A possible reason for the distortion of the spherical shape in the case of particles with non-filled electron shells has been established.¹⁷⁹ It is similar to the Jahn–Teller effect:¹⁵⁸ due to the high degeneracy of the quantum electron levels with respect to l , the energy of electrons in nearly spherical particles becomes a non-analytical function of the surface area of the cluster S . The change in the surface area upon the deformation of a spherical particle increases its surface energy, on the one hand, and decreases the energy of electrons due to splitting of the upper electron level E_{nl} (n is the principal quantum number), on the other hand. The resultant change in energy is found from the equation¹⁷⁹

$$\delta E = \gamma \delta S - g(n, l, m_0)(\delta S)^{1/2},$$

where $g(n, l, m_0) > 0$ is a function of the principal and orbital quantum numbers and of the number of electrons m_0 in the outer shell, and δS is the change of the surface area of the particle upon deformation. The minimisation of the cluster energy determines the equilibrium deformation. According to an estimate made for cesium clusters, in the case of clusters with a size of 5 nm, the relative deformation can reach 10%. The same effect determines the size oscillations of the particle shape.

The possibility of a rearrangement of the ion core (not only of the change in the particle shape) also affects substantially cluster characteristics. Ivanov *et al.*^{180, 181} carried out calculations for clusters in terms of the optimised jellium model they proposed. In this model, the distribution of the positive charge in the jellium was regarded as unknown *a priori* and was determined from the condition of the minimum total energy. The possibility of rearrangement of both the electronic energy spectrum and the ion core was assumed in the calculations. The calculations showed that the internal structure of a jellium-like core is formed in the cluster bulk and the positive charge is distributed non-uniformly in space. As a consequence, regions of maximum and minimum jellium density appear; they correspond to the equilibrium positions of ions in the lattice of a polyatomic cluster. The electron levels also rearrange, this effect being the most pronounced for clusters with filled shells. The magic numbers corresponding to the most stable electronic configurations of clusters with filled shells are also reproduced. For example, $N = 40$ is matched by the configuration $1s^2 1p^6 1d^{10} 2s^2 1f^{14} 2p^6$. The energy difference between optimised and non-optimised cluster models is 0.1 eV per atom and remains nearly constant for clusters with different sizes. The dependence of the average cluster radius on the number of atoms also changes substantially on passing from the non-optimised to the optimised model — this dependence becomes non-monotonic and local minima at $N = 8, 20, 40, 58$, etc. appear on the corresponding curve; *i.e.* clusters with filled shells are more compact.

The method of the density functional, including that as applied to clusters, can easily be extended to non-zero temperatures.^{182–185} When the temperature differs from zero, Eqn (8) has the form

$$\rho(\mathbf{r}) = \sum_i \phi_i^2 f(E_i - \mu). \quad (48)$$

Here,

$$f(E_i - \mu) = \left(1 + \exp \frac{E_i - \mu}{kT} \right)^{-1}, \quad (49)$$

μ is the chemical potential, k is the Boltzmann constant, T is temperature, and the function $f(E_i - \mu)$ should satisfy the condition

$$\sum_i f(E_i - \mu) = N, \quad (50)$$

where summation involves all the single-electron states.

For finite temperatures, Eqns (37)–(39) and (48)–(50) can be used to determine a single-electron energy spectrum of a system (e.g., cluster), the electron density distribution in the system as well as the chemical potential and the occupancy numbers of electron states.

The temperature also influences substantially the structure of clusters. The distribution function of the levels located near μ changes markedly even at relatively low temperatures: it decreases for higher occupied levels and becomes non-zero for levels located above μ . The temperature variation of the occupancy numbers for 3d, 4s and 1k levels closest to the chemical potential level in the Na₁₉₆ cluster has been calculated.¹⁸⁶ It was shown that the transition of electrons to higher energy levels starts even at temperatures appreciably (several times) lower than the values corresponding to the difference in energy between the levels. Moreover, at $T = 300$ K, the occupancy of the 1k level, which lies above the 4s level, proves to be greater than that of 4s. The pattern of variation of the chemical potential vs. temperature is equally complicated. In the clusters with $N = 18$, the chemical potential increases, while in clusters with $N = 40$, it, conversely, decreases with an increase in temperature. The complex temperature dependence of the chemical potential is due to the fact that it is determined by the orbital quantum numbers of the energy levels between which redistribution of electrons takes place.¹⁸⁶

For finite temperatures, the deviation of the cluster shape from spherical is more significant than at $T = 0$ K. In the former case, the loss of sphericity can result not only from deformation of electron shells but also from thermal excitations of the ion core. However, the relevant calculations are associated with substantial procedural difficulties and have not been performed yet.

2. Thermodynamics of electrons in small particles

The thermodynamics of electrons in small particles have been studied fairly comprehensively by Denton *et al.*,¹⁷³ who calculated heat capacities and magnetic susceptibilities of particles for various ensembles. The thermodynamic characteristics of particles were found to depend on the number of electrons in them. The results of standard calculations with allowance for the level statistics are given in Table 1.

It can be seen from the Table that ‘repulsion’ of the energy levels changes in form the pattern of the temperature variation of the heat capacity of small particles. Instead of the linear dependence, typical of bulk samples,¹⁸⁷ a non-linear dependence correlated with the degree of repulsion of the levels is observed. The enhancement of the temperature dependence of heat capacity for low T values is due to the decrease in the probability of close arrangement of levels — the smaller the number of close levels, the smaller the number of electrons able to pass to higher levels on thermal excitation and the lower the heat capacity.

The difference between the heat capacities of particles with even and odd numbers of electrons is not as pronounced as the difference in the magnetic susceptibilities. For even numbers of

Table 1. Heat capacities and magnetic susceptibilities of particles in various ensembles.

Ensemble	N is even	N is odd
Heat capacity (in k units)		
Poisson	$5.02(kT/\Delta_m)$	$3.29(kT/\Delta_m)$
Orthogonal	$3.02 \times 10(kT/\Delta_m)^2$	$1.78 \times 10(kT/\Delta_m)^2$
Symplectic	$3.18 \times 10^4(kT/\Delta_m)^5$	$1.64 \times 10^4(kT/\Delta_m)^5$
Unitary	$5.88 \times 10^2(kT/\Delta_m)^3$	$5.88 \times 10^2(kT/\Delta_m)^3$
Magnetic susceptibility		
Poisson	$3.04 \left(\frac{1}{2} g\mu_B \right)^2 / \Delta_m$	—
Orthogonal	$7.63 \left(\frac{1}{2} g\mu_B \right)^2 kT / (\Delta_m)^2$	$\left(\frac{1}{2} g\mu_B \right)^2 / kT$
Symplectic	$2.02 \times 10^3 \left(\frac{1}{2} g\mu_B \right)^2 (kT/\Delta_m)^4 / \Delta_m$	—

Note. Generally accepted designations: g is the gyromagnetic ratio, Δ_m is the average distance between electron levels.

electrons, the magnetic susceptibility tends to zero at $T \rightarrow 0$ for orthogonal and symplectic ensembles; this is explained by pairing of electrons on separated levels. In the case of the Poisson ensemble, the levels do not repel one another and, with a finite probability, they can be located rather closely; this results in a temperature-independent magnetic susceptibility. For systems with odd numbers of electrons, the magnetic susceptibility of any ensemble, conversely, tends to infinity. This pattern of susceptibility is due to the presence in the upper level of an unpaired electron, which accounts for the sharp increase in the susceptibility on a decrease in temperature.

Until recently, it has been impossible to verify these patterns of temperature dependence of the magnetic susceptibility and heat capacity by direct experiments because the systems prepared contained particles with both even and odd numbers of electrons. As a consequence, only ensemble-average characteristics were observed in experiments. It should be noted, however, that the magnetic susceptibilities of particles with even and odd numbers of electrons have been measured^{3,4} in NMR experiments: the temperature dependence of susceptibility for particles with different numbers of electrons, even when they are present simultaneously in the system, can be determined from the Knight shift.

In recent years, substantial interest in the studies of the heat capacity and magnetic susceptibility of small particles has revived, which is due to the above-mentioned possibility of preparing metallic nanoparticles with a virtually definite number of atoms by the method developed in a series of studies.^{78–89} The advances in the synthesis of nanoparticles permitted experimental verification of the correctness of the theory of their thermodynamic properties. Experiments of this type have been described by Volokitin *et al.*,^{188,189} who carried out a detailed investigation of the thermodynamic characteristics of particles with different numbers of atoms (and, correspondingly, electrons). The experiments were performed with palladium clusters containing 561, 1415, 1740 and 2057 atoms as well as with larger clusters isolated from one another in the samples by ligand shells. The electronic heat capacity and magnetic susceptibility of metal particles were studied as functions of particle size and temperature in the range from 0.05 to 10 K, in which the effects of quantisation of the electron movement should be visible.

Figure 3 shows the temperature dependences of the specific heat capacity (C) of nanoparticles of various sizes and of bulk samples. It can be seen that the plots for nanoparticles of different sizes do not coincide at $T < 2$ K. The deviation from the data for bulk substances increases as the particle size decreases. The results of processing of experimental data by normalisation of the

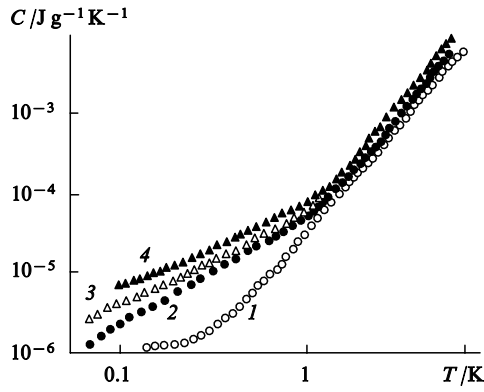


Figure 3. Temperature dependence of the specific heat capacity (C) for palladium clusters with five (1), seven (2) and eight (3) atomic shells and for clusters containing more than 10^5 atoms (4).¹⁸⁹

dependences to characteristics of the particles of different dimensions are presented in Fig. 4. The same figure shows the theoretical $C(T)$ plot for the orthogonal ensemble. It can be seen from the figure that the theory reliably reproduces experimental data, which point unambiguously to quantisation of the electron levels in small particles.

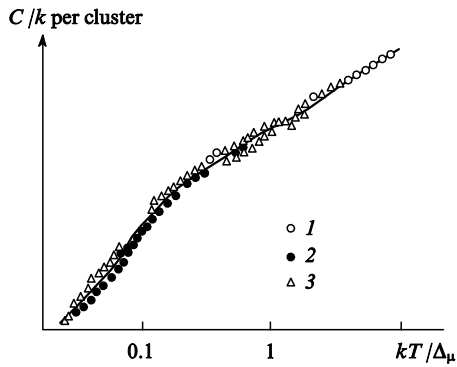


Figure 4. Normalised temperature dependences of the heat capacity for particles with different sizes.¹⁸⁹ The continuous curve is the calculated dependence for the orthogonal ensemble.

Good agreement between theoretical and experimental results was also obtained for magnetic susceptibility measurements (Fig. 5). These experiments are actually the first studies in which

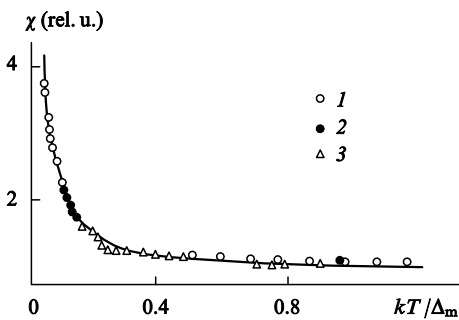


Figure 5. Normalised temperature dependences of the magnetic susceptibility (χ) for nanoparticles with five (1), seven (2) and eight (3) atomic shells.¹⁸⁹ The continuous curve is the calculated dependence for the orthogonal ensemble with equal percentages (50%) of particles with even and odd numbers of electrons.

the quantum nature of electrons in small particles was demonstrated in an explicit form.

3. Disjoining pressure in liquid metallic films

The stability of free liquid films is due to a positive disjoining pressure $\Pi(H)$,¹⁹⁰ which prevents a decrease in their thickness H . The disjoining pressure $\Pi(H)$ is the difference between the pressure normal to the film surface and the pressure in the bulk phase contacting with the film.¹⁹⁰ The pressure difference arises due to the surface forces when the boundary layers of the two phases overlap.

It is commonly supposed¹⁹⁰ that the disjoining pressure in single-component systems is always negative; therefore, free films of neat substances cannot be stable. However, it has been shown^{61, 191–193} that this rule can be violated for liquid metal films. The appearance of a positive component of disjoining pressure is related to the quantisation of the electron movement in thin films. The physical nature of this component of disjoining pressure is rather simple. According to the Heisenberg uncertainty principle, the component of the electronic momentum directed at the right angle to the surface cannot be smaller than $\hbar/H$. As a consequence, the minimum possible energy of electrons in the film amounts to $\hbar^2/2mH^2$. Owing to this restriction, the energy of each electron in the film increases, due to degeneracy, by a value approximately equal to the above value, even for a continuous spectrum of electron energies. Thus, the change in the density of the total energy of electrons is

$$\Delta E \sim \frac{N\hbar^2}{2mH^2V},$$

where N is the number of electrons in the film and V is the film volume. The pressure of the degenerate electron gas is proportional to the energy density. As a result, the pressure of electrons in thin films increases with respect to the pressure in the bulk by the value

$$\Pi(H) \sim \frac{N\hbar^2}{2mH^2V}.$$

The electron component of the disjoining pressure in thin films was calculated by two methods;^{161, 192, 193} in one method, the model of a potential well with infinitely high walls was used, while the other method was based on the phenomenological model considered above in which the derivative of the electronic wave function on the film surface was specified. In the former case, the film was found to be absolutely stable, while in the latter case, film stability was determined by the nature of the surrounding medium. Let us consider results obtained by Roldughin and Deryagin.^{161, 193} According to these studies,

$$\Pi(H) = E_{0F} \frac{N}{V} R^2 \times \left[\chi_s(\lambda_s) + \frac{2}{R} \exp\left(-\frac{\gamma}{\sqrt{E_{0F}}}\right) \sin\left(2\sqrt{\frac{2mE_{0F}}{\hbar^2}}H + \varphi_0\right) \right], \quad (51)$$

where E_{0F} is the Fermi energy for a bulk sample

$$R = \frac{1}{H} \left(\frac{V}{3\pi^2 N} \right)^{1/3},$$

γ is a value characterising the width of electron levels¹⁷³ and $\chi_s(\lambda_s)$, φ_0 are functions of the parameter λ appearing in the boundary conditions. For the λ value corresponding to a potential well with infinitely high walls, expression (51) for $\Pi(H)$ transforms into the relation derived in another publication.¹⁹² The function χ can be both positive and negative, its sign determining the sign of the disjoining pressure. The last term in relation (51) is insignificant for determination of the film stability because it represents a rapidly oscillating value. This term is due to the discrete character of the electron levels in thin films.

Let us clarify the nature of the change of the sign of disjoining pressure in a thin film following the change in the parameter λ_s , which describes the behaviour of the electronic wave function and, hence, the electron density near the geometrical surface of the film. Actually, λ_s specifies the distance by which electrons are 'allowed' to go out into the external environment. If electrons can easily leave the geometrical surface of the film, their effective density in the film decreases. The decrease in the effective density diminishes the Fermi energy and, as a consequence, the pressure of electrons in the film. Thus, the quantisation effect mentioned above, which ensures a positive disjoining pressure, can be counterbalanced by a decrease in the electron density. This implies that the stability of liquid metallic films is determined to a large extent by the nature of the environment.

Experiments confirm this conclusion. For example, the stability of mercury films adjoining various organic liquids has been studied.^{194, 195} It was found that in octane, mercury films exist for infinitely long periods, whereas in decane, the lifetime of the films does not exceed 1 min; the lifetime in toluene is ~ 1 s.

V. Optical properties of small particles

Nanometer particles have unique optical properties, which are used both for scientific and practical purposes. The optical characteristics of these particles are determined by conventional spectroscopic methods;^{3, 196} therefore, the vast majority of studies devoted to a particular method for the preparation of nanoparticles contain sections devoted to their absorption spectra. Optical spectra provide fundamental information on the electronic structure of small metal particles. In particular, investigation into optical spectra allows one to follow the variation of electronic properties on passing from bulk samples to small particles.

The unique optical properties of small particles are finding application in the design of optical filters, markers of biomacromolecules, reversible photosensitive monochromatic glasses, optical switches and optical traps and for surface enhancement of Raman light scattering spectra.

Absorption spectra of small metal particles have an intense broad band which is missing from the spectra of bulk samples. This band is associated with the collective excitation of the conduction electrons (surface plasmons); its occurrence in the visible region results in a unique colour spectrum of dilute colloidal dispersions of noble, alkaline earth and rare earth metal particles.

The nature of plasmon absorption is fairly simple. Under the influence of the electric field of the incident radiation, the conduction electrons in the particle are displaced with respect to the positively charged ion core. This displacement is cooperative, *i.e.* the movement of electrons is phase matched. The displacement of electrons gives rise to a force which acts to return the electrons to the equilibrium position. The returning force is proportional to the displacement, as for a typical oscillator; therefore, one can speak about the presence of a natural frequency of cooperative oscillations of electrons in a particle. The coincidence of the natural frequency of the cooperative electron oscillations with the frequency of the external field gives rise to a resonance effect related to the excitation of natural oscillations of electrons. In accordance with the symmetry of the spatial size distribution, the resonance cooperative movement of electrons can be represented as an infinite set of separate modes, namely, dipole, quadrupole and other modes. The description of the cooperative movement of electrons in terms of quantum mechanics results in the notion of elementary excitations — plasmons having the energy $\hbar\omega_0$, where ω_0 is the natural frequency of cooperative oscillations. The lifetime of plasmons is short, it is about tens of femtoseconds.

Although the optical properties of nanoparticles are determined by quantum effects, they are well reproduced in terms of the Mie theory,^{3, 196} in which the optical properties of spherical metal particles in dielectric matrices are interpreted within the frame-

work of classical electrodynamics. The response of a particle is described by Maxwell equations and the corresponding boundary conditions. Optical resonance (Mie resonance) also appears in terms of the Mie theory, due to the cooperative excitation of the electron plasma. The properties of the particle material do not appear in the Mie theory in an explicit form; it is assumed that they can be described using the complex dielectric constant, as in the case of bulk solids.

The profile of the absorption band near the Mie resonance for a nanoparticle is a Lorentzian curve characterised by the position and width of the $\hbar\omega_0$ peak. For particles with a size much smaller than the radiation wavelength, the resonance frequency is described by the expression¹⁹⁶

$$\omega_0 = \left(\frac{n e^2}{\varepsilon_0 m_e} \right)^{1/2} (2\varepsilon_m + 1 + \chi_{li})^{-1/2}, \quad (52)$$

where n is the density of electrons, ε_0 is the electric constant, m_e is the effective mass of the conduction electrons, ε_m is the real part of the dielectric constant of the medium, and χ_{li} is its component related to the band–band transitions in the particle.

It can be seen from Eqn (52) that the position of the resonance depends not only on the parameters of the conduction electrons but also on band–band transitions and electron–hole excitations.

The resonance width is determined by the relation¹⁹⁶

$$\Gamma_{r0} = 2\varepsilon_2(\omega) \left[\left(\frac{\partial \varepsilon_1}{\partial \omega} \right)^2 + \left(\frac{\partial \varepsilon_2}{\partial \omega} \right)^2 \right]^{-1/2}, \quad (53)$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of the dielectric constant of the particle and ω is the current radiation frequency.

According to the Mie theory, starting from some size of the particles (about one-tenth of the radiation wavelength), the position and the width of the absorption band no longer depend on the particle size. However, a substantial shift of the resonance and the broadening of bands following a decrease in the particle size was observed in experiments.

The relevant theoretical models have been considered.¹⁹⁷ The greatest contribution to the variation of the position of the peak as a function of particle size is made by the changes in the average density of electrons in the particles, in the effective mass of electrons and in the susceptibility related to the band–band transitions. However, for typical values of these parameters, the size corrections are usually too small. Therefore, it was assumed that for small particles, collisions of electrons with the surface of particles should be significant (the mean free path in gold is 20 nm). This hypothesis provided an interpretation of the spectra of relatively large particles (> 3 nm for gold) but proved inapplicable to smaller particles. It is clear that the classical views on free electrons become invalid for small particles and quantum size effects should be taken into account. Nevertheless, no demonstrations of these effects have yet been identified unambiguously in the optical properties of small particles, although they show themselves in other properties;^{175, 176} in particular, they are manifested as the change in the conductivity of single particles.^{198, 199} This might be due to the use in experiments of particle ensembles having different sizes and shapes.

An attempt to overcome this difficulty has been undertaken by Alvarez *et al.*,²⁰⁰ who studied the spectra of gold nanocrystals stabilised by *n*-alkanethiolates in toluene. The dimensions of metal particles varied from 1.4 to 3.2 nm (70 to 800 Au atoms); special methods for separation of narrow fractions of particles were used for this purpose. It was found that the absorption spectrum depends slightly on the length of the alkyl chain in the stabilising agent and that the characteristic band (2.4 eV) is broadened upon a decrease in the particle size and virtually disappears for 2 nm particles. A band corresponding to resonance transitions (1.7 eV) was identified and the presence of step structures in the absorption spectrum of small clusters (smaller

than 2 nm) was demonstrated. This spectral feature was attributed to the quantum size effects caused by transitions of electrons from the conduction bands to the discrete levels located above the Fermi level.

It should be noted in this connection that the assumption concerning the change in the optical parameters of gold for particles with a size of 3 nm has also been made previously.²⁰¹ It can be expected that 2 nm is an intermediate size in passing from continuous to atomic structure for particles passivated by thiolates. The transition of a nanoparticle to the metallic state is manifested especially clearly in the absorption spectra (see, for example, Refs 202 and 203).

For the width of the plasmon absorption band for nanoparticles, described by a continuum model, the following expression was obtained:¹⁹⁷

$$\Gamma_r = \Gamma_{r0} + \frac{2\omega_0^2}{\omega^3} v_F \left[\left(\frac{\partial \epsilon_1}{\partial \omega} \right)^2 + \left(\frac{\partial \epsilon_2}{\partial \omega} \right)^2 \right]^{-1/2} \frac{A}{R}, \quad (54)$$

where v_F is the Fermi velocity of electrons, A is a constant, R is the particle radius.

The corresponding dependence of the width of the absorption band on the size of particles has been confirmed experimentally.²⁰⁴ The magnitude of the constant A depends substantially on the nature of the medium surrounding the particles and on the presence and parameters of the adsorbates.²⁰⁵ The medium or adsorbed molecules (electron donors or acceptors) can change markedly the effective concentration of electrons in the particle, resulting in a shift in the resonance and a change in the band width. Apart from this static shift of the resonance and the change in the width of the absorption band, dynamic effects related to the transfer of electrons from the Fermi surface to the adjacent levels of adsorbed molecules or the environment are also possible.

The effects of this type have been studied;^{206–209} effects of adsorption of $S_2O_3^{2-}$ and halide ions on silver particles^{206, 207, 209} and $S_2O_3^{2-}$ ions and pyridine molecules²⁰⁸ on silver particles and on the particles of a copper–silver alloy in an aqueous solution were established. The resulting absorption spectra were processed in terms of the Mie theory; the concentration of conduction electrons in the particles and attenuation coefficients of plasmons were found as functions of adsorption of the corresponding ions. Experiments showed that for 3–5-nm silver and bimetallic particles, the concentration of conduction electrons increases by approximately 10% and 5%, respectively, and the absorption coefficient increases 2- and 1.6-fold, respectively. The increase in the electron density was explained by its movement from the adsorbate to the metal, while the increase in the attenuation coefficient was attributed to the increase in the cross-section of electron scattering on the surface defects which have captured the adsorbate molecules.

It should be mentioned that the Mie theory with appropriate modification of the parameters permits one to describe virtually all the available experimental data on absorption spectra (naturally, except for those for very small particles).²¹⁰ For this reason, theoretical description of the optical characteristics of particles lags substantially behind experimental studies. Simultaneously, the Mie theory has been developed to become more precise and more general in order to go beyond the limits of the approximations used. In particular, investigation into the influence of the shape and the state of the surface of particles on the optical properties have been started. In early studies, simple shapes of particles were chosen — spheres,^{211–213} cylinders or parallelepipeds, because calculations were carried out by quantum-mechanics methods, which imposed certain demands on the shape of particles that enable exact solution of the Schrödinger equation. In these studies, electric absorption, stipulated by the electrical conductivity of particles (determination of which was the object of the studies), was calculated. In the case of particles with a size exceeding the mean free path of electrons, the conductivity is related to the bulk conductivity of the metal; hence, the calcu-

lation of electric absorption is actually reduced to determination of the electric field in the particle.

Magnetic absorption by spherical particles has been studied.²¹⁴ The calculations were based on the solution of the kinetic equation for electrons in terms of the Bhatnagar–Gross–Krook model. The same model was used in another study²¹⁵ to calculate the electronic and magnetic absorption of spheroidal particles. Particles with sizes both larger and smaller than the mean free path of electrons were considered. It was shown that the total absorption and the ratio of electronic to magnetic absorption depend appreciably on the shape of particles and polarisation of the incident electromagnetic wave; these values can change by several orders of magnitude with a fixed particle volume.

In the Mie theory and in other theoretical approaches, the particles are assumed to have a regular shape and smooth surface. However, in practice, this is not always true. In particular, clusters applied on a substrate are shaped like deformed spheroids rather than like spheres.²¹⁶ In addition, on the surface of particles, atoms can occupy positions with different coordination numbers; in particular, they can be rather low, which means roughness at the atomic level. As a result, new channels for light absorption by particles appear.

Experiments^{217, 218} and theoretical calculations²¹⁹ showed that the state of the particle surface is really important for light absorption. Electron resonances localised in the near-surface layer are significant when they overlap with the surface plasmons. In this case, they are excited very rapidly because excitation of a plasmon is accompanied by enhancement of the field on the surface.

Absorption on the surface of small particles has been observed experimentally;²²⁰ for this purpose, a special method for the separation of surface and bulk absorption was used. Metal particles shown²²¹ to have a smooth surface and surface electronic states were applied on a transparent substrate from the vapour phase at 100 K. The particles were exposed to pulse laser radiation, which excited the electrons on the surface and in the bulk. Upon attenuation of the excitations, the temperature of the sample rose, which caused desorption of atoms from the surface. The velocities of the desorbed atoms were measured in order to determine the temperature of the particles. From the difference between the temperatures, the energy absorbed by the particles was found. The surface and bulk excitations were separated by repeating this procedure for particles the roughness of which had been removed by heating and slow quenching. The experiments with sodium particles supported on the surface of quartz glass demonstrated that the surface contribution to the absorption is equal to 32% for clusters with a size of 21 nm.

In recent years, the interest in the optical properties of colloidal dispersions of bimetallic particles has markedly enhanced. Various pairs of metals have been studied.^{222–227} Bimetallic particles containing silver and mercury received particular attention. Both metals are characterised by sharp absorption bands corresponding to surface plasmons and located rather closely together, *viz.* at 380 nm for silver in water and at 300 nm for mercury.²²⁸ Bimetallic particles of this type having different compositions have been prepared.²²⁹ Investigation of their absorption spectra showed that the plasmon resonance bands shift to shorter wavelengths as the content of mercury in the drops increases. The variation of the absorption spectra during the preparation of the colloids was studied. Mercury drops were found to be formed initially during the reduction of metals; silver ions are reduced simultaneously. Then an amalgam is formed in which silver particles occur in the drops of mercury. The colloid is stable if the Hg : Ag ratio is greater than 2. Otherwise, it starts to opalesce and sedimentation occurs. The formation of the amalgam influences the absorption spectrum: the plasmon resonance shifts towards longer wavelengths.

The non-linear optical properties of the nanoparticle ensembles proved unexpected; they are influenced by secondary cooperative effects caused by interaction of excited nanoparticles.

Abnormal enhancement of hyper-Rayleigh scattering in dispersions of gold nanoparticles has been observed.^{230, 231} In a study of the influence of high radiation doses on silver nanoparticles, the presence of a limiting transmission threshold was established;²³² *i.e.* dispersion resulted in an increase in the light absorbance due to non-linear effects. This enhancement was attributed to photochemical processes which have started on the particle surface. Yet another cooperative effect was found in another study.²³³ It was found that the intensity of the surface enhanced Raman scattering increases due to participation of surface ensembles of particles; this effect depends on the composition of particles in a rather complex manner (the experiments were carried out with nanoparticles of gold and silver).

VI. The influence of radiation on the stability of nanoparticles

The optical properties of nanoparticles can be changed by various types of treatment of the colloidal system, for example, by introducing stabilising or destabilising additives, by changing the temperature and also by irradiation of the system. A usual result of this types of treatment is the change in the aggregation state of the colloidal dispersion.

If the particles form aggregates,^{234, 235} the corresponding plasmon band either shifts towards longer wavelengths or becomes broader. However, when the colloidal particles are aggregated, the distribution of particles in the aggregate does not correspond to a close packing. In most cases, aggregation yields fractal structures having one or another fractal dimension, depending on the aggregation conditions.^{236–238} A theory of the optical properties of fractal clusters has been developed;^{239, 240} it was shown that the presence of close neighbours of a particle in the aggregate changes the frequency of optical resonances of the particle and causes band broadening. The change in the frequency and band broadening are due to the dipole–dipole interactions between the light-induced dipole moments of particles. This effect underlies a method for the estimation of the degree of aggregation of colloidal systems, which allows one to monitor the evolution of colloids under complex conditions (see, for example, Ref. 202).

Hasegawa *et al.*²⁴¹ studied the light-induced variations in the stability of colloidal dispersions of ultrasmall particles. They investigated various metal particles dispersed in various organic media. It was found that a sol of gold in chloroform starts to sediment 4 h after irradiation by the light of a mercury lamp, whereas in the dark, it remains stable for a year. Thus, under the influence of light, the rate of coagulation increases by a factor of 1000.

Similar results were obtained for gold particles in water,²⁴² the rate of coagulation being dependent on the radiation frequency. The maximum rate was observed at the frequency corresponding to the Mie resonance. It has been suggested²⁴³ that coagulation is caused by the dipole interaction of particles, which is enhanced by external radiation.

A more detailed study has been performed by Satoh *et al.*¹³ The experiments were carried out with a gold sol prepared by vaporisation followed by deposition from the flow into an organic liquid without using surfactants or stabilisers. Gold sols in acetone, ethanol, propan-2-ol and chloroform as solvents were prepared. The changes in the absorption spectrum on exposure to the light of a mercury lamp and on heating the dispersion were determined. The initial peak (surface plasmon) at a wavelength of 523 nm was found to be broadened and to disappear; the band at 270 nm becomes more intense and a new band at 840 nm appears. The shift of the plasmon peak was attributed to the dipole–dipole interaction of particles in the aggregates.²³⁴ After 20 h of irradiation, complete sedimentation of the aggregates occurred and re-dispersion was impossible. The rate of coagulation depended on the solvent used.

It was found by electron microscopy that nanoparticles form fractal aggregates with a dimension of 1.7, which corresponds to

the diffusion-controlled aggregation model (at an initial stage, unidimensional chains are formed in the system). It was assumed that coagulation is due to the enhancement of the van der Waals attraction caused by the presence of induced dipoles. To verify this assumption, the effect of radiation with different wavelengths on the particles was studied. Coagulation was found to take place even on exposure to visible light. However, UV radiation markedly enhances coagulation. To explain the effect of the radiation wavelength on the rate of aggregation, it was suggested that the instability of the sol (in addition to the increase in the van der Waals interaction mentioned above), can also be related to the change in the Coulomb repulsion as a result of the change of the surface charge due to photochemical processes.

In order to verify this hypothesis, in addition to the measurements of the stability of a dispersion of gold particles in water and propan-2-ol under the action of radiation, their ζ potentials were measured.¹⁴ The coagulation rate was determined not only from the shift of absorption but also by electron microscopy using a special procedure. The relationship between the rate of coagulation and the change in the ζ potential of the particle caused by the addition of a salt was studied. On exposure to radiation, the ζ potential decreased from -45 to -65 mV. The increase in the absolute magnitude of ζ indicates enhancement of the Coulomb repulsion between the particles; thus, this cannot account for the loss of stability of colloidal nanoparticles.

Karpov *et al.*,^{244–246} who studied silver sols, proposed a somewhat different interpretation for photostimulated aggregation. The aggregation of particles was detected from the absorption spectra of colloids. It was established that the rate of aggregation increases by a factor of 10^{10} upon irradiation;²⁴⁷ it was suggested that the acceleration of aggregation was based on the photoeffect.

The proposed mechanism is as follows. Irradiation of a colloid gives rise to oppositely charged particles, due to exchange of the electric charges arising upon photoemission. The exchange proceeds through the dispersion medium; it is due to the fact that the Fermi energy of particles depends on their size and results in equalisation of the electrochemical potentials of particles of different sizes. The long-range electrostatic forces arising after the exchange play a crucial role in the fact that particles approach one another to distances at which van der Waals forces start to show themselves.

The possibility of formation of a contact potential between quantum-size systems of the same nature has been indicated.^{191, 192} This effect was attributed to the shift of the chemical potential under conditions where the movement of electrons is confined by the metal film surface. At the thermodynamic equilibrium, electrons are redistributed between systems of different sizes to ensure equal electrochemical potentials. The effect of this distribution of electrons between nanoparticles has been used¹⁶² to introduce attractive forces between the particles in an equilibrated polydisperse system.

If the process of aggregation of nanoparticles is underlain by photoelectric emission, a 'red boundary' of the process should exist. The variation of the rate of photoaggregation of a silver hydrosol has been studied experimentally by exposure of identical samples to radiation in the range from 366 to 1050 nm.²⁴⁶ The experiments showed that the rate of photoaggregation depends on the radiation wavelength and that a red boundary for the process does exist. However, when the radiation power is rather high, two-photon processes, which shift this boundary, start to play a noticeable role. An interesting feature of photoaggregation has been noted: a higher initial aggregation of particles implies a lower exposure dose required to increase aggregation by the same amount. In a freshly prepared sol, the process of photoaggregation does not start until a threshold radiation intensity is reached, because the sol does not contain spontaneously formed aggregates of two or three particles needed as seeds for photostimulated aggregation.²⁴⁶

The presence of a threshold irradiation dose in the process of destabilisation of colloidal silver sols has also been noted in another study,⁹³ in which irradiation was carried out by electrons (5 MeV) and γ -quanta (^{60}Co as the source). The irradiation by electrons was pulsed (pulse duration 2 μs). The coagulation of particles was indicated by changes in the optical absorption spectra. No changes were detected after 50 pulses. However, in the case of 60–70 pulses, the intensity of the major absorption band sharply decreased, while its width increased. An appreciable increase in the light scattering by the colloidal dispersion was also observed. A critical irradiation dose was also found to exist when γ -quanta were used. The loss of stability of sols in these experiments was attributed to the neutralisation of the particle charge due to the reduction of sorbed silver ions under the action of radiation; this destroys the double electric layer at the particle boundary. The specificity of the electron irradiation was in that it ‘delivered’ electrons, and the charge on the silver particle decreased upon absorption of these electrons. A similar view on the reasons for destabilisation of the nanoparticle sol on exposure to γ -radiation has been expressed in other studies;^{248–251} regularities of the formation of fractal aggregates from silver nanoparticles have been investigated.²⁵¹

VII. Relaxation of electrons in small particles

Direct measurements of the dynamics of electrons in small particles became possible, most of all, owing to the development of ultrafast laser equipment. Absorption spectroscopy is used most often. Short (100 fs) laser pulses are employed to bring electrons into excited states, the relaxation of which is observed by means of the second, probing laser beam. The dynamics of relaxation was determined from the time variation of the absorption between two successive excitations of the system. The variation of transparency with time, related to the restoration of the ground state of the system, is also measured in some cases. The dynamics of electrons in semiconductor particles has been considered in a review;⁷ therefore, we do not discuss it here.

Metal particles differ substantially from semiconductor particles. The main difference is in the structure of electron energy levels. The forbidden gap, which plays a fundamental role in semiconductor particles, is lacking in the case of metals (Fig. 6). At ordinary temperatures, the distance between the electron levels in metal particles can be considered to be relatively small and their optical properties differ little from those of bulk metal samples.¹⁷⁵ Therefore, the electron dynamics in small metal particles markedly differs from that in semiconductor particles.

For small metal particles, only the optical absorption and structural properties have long been studied,^{252–256} whereas the study of electron dynamics has started only recently. The regularities of electron relaxation for times longer than 2 ps have been elucidated.²⁵⁷ The first femtosecond study of relaxation was performed by Roberti *et al.*²⁵⁸ in relation to a dispersion of gold

clusters in water. Subsequently, similar studies^{259, 260} were carried out for silver and platinum nanoparticles in aqueous and organic media.

The investigations showed that for silver and gold particles, relaxation at early stages is determined by the electron–phonon interaction, the relaxation times being 2.5 and 7 ps, respectively. These times are longer than the corresponding relaxation times for bulk samples (670 fs for silver and 1 ps for gold).^{261, 262} The retardation of electron relaxation in nanoparticles was ascribed²⁵⁹ to the decrease in the electron–phonon interaction. This decrease has been predicted theoretically,²⁶³ the relaxation time for gold particles corresponding to that measured for island films.²⁶⁴ Similar femtosecond studies have been carried out for gold^{265–270} and zinc²⁷¹ nanoparticles. Studies of gold particles in glass matrices resulted in a relaxation time of 4 ps.²⁶⁶

It was also demonstrated that the difference between the relaxation times for particles having the same size can be due to the use of different stabilising agents. Thus it was found²⁶⁰ that the relaxation times for the same gold particles (18 nm) in water and cyclohexane are 7 and 3.5 ps, respectively.

For tin particles, the dependence of the relaxation time on the particle size was attributed²⁷¹ to the effect of electron collisions with the particle surface. These results stimulated investigations into this dependence for gold particles with strictly specified dimensions. Thus it was found²⁷² that the relaxation time (τ) for the Au_{55} particle is 1 ps and that for Au_{13} is 300 ps. The electron relaxation for the Au_{55} cluster with a diameter of 2 nm proceeds much faster than that in larger (14–40 nm) particles (Fig. 7), for which the relaxation time is 7 ps. The experimental results are described by a phenomenological formula²⁷³

$$\frac{1}{\tau} = \frac{aR^\alpha}{\tau_b} + \frac{bv_F}{R}, \quad (55)$$

where a , b are constants, τ_b is the bulk relaxation time, v_F is the Fermi velocity, R is the particle radius and α is an integer which can be found from the corresponding theoretical model.²⁶³

According to Eqn (55), as the particle size decreases, the relaxation time first increases, because the first term (normalised electron–phonon interaction) predominates. When the particle size further decreases, the second term starts to predominate and the relaxation time diminishes.

The same pattern of variation follows from the measurements of electron relaxation in platinum particles.²⁷³ However, the data for the Au_{13} clusters do not fit in this regularity. Thus, formula (55) is inapplicable to small clusters, apparently, due to the loss of metallic properties by the clusters (in particular, Au_{13}). This fact is also confirmed by measurements of the absorption spectra of these clusters,^{272, 274} in which many new bands appear. From this it follows that the transition from bulk properties to molecular properties for gold clusters takes place in the range from 55 to 13 atoms.

Deviations from the dependence given by relation (55) are also observed upon an increase in the pumping radiation

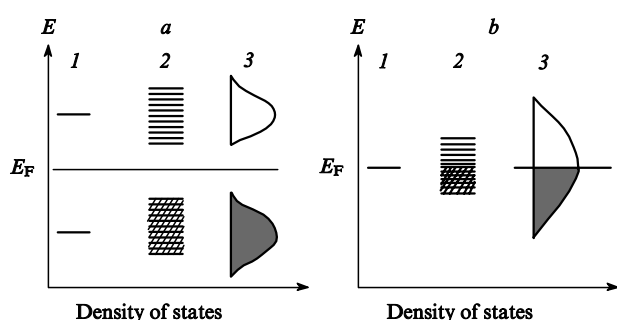


Figure 6. Diagrams of energy levels in semiconductors (a) and metals (b). (1) atoms, (2) small particles, (3) bulk samples. Occupied levels are cross-hatched, E_F is the Fermi level.

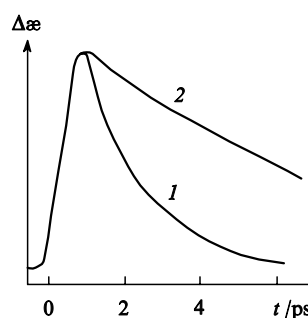


Figure 7. Change in the optical absorption coefficient (ϵ) vs. time for excited Au_{55} particles (1) and gold particles with a dimension of 15 nm (2).²⁷²

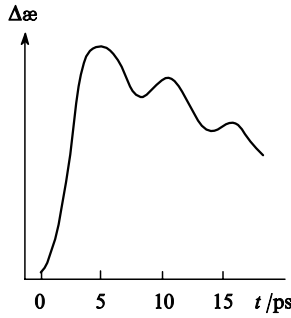


Figure 8. Change in the optical absorption coefficient vs. time for excited gold nanoparticles with a dimension of 15 nm.²⁷⁰

power.^{268, 270, 275} In this case, the time of electron relaxation increases linearly with the intensity of the pumping radiation power, which is due to the heating of electrons and ‘detachment’ of their temperature from the temperature of the ion lattice.

Yet another interesting phenomenon was discovered in the studies cited above, namely, modulation of the absorption of the probing radiation (Fig. 8). The modulation was found for gold particles with a size from 14 to 17 nm. It was found that the modulation frequency did not correspond to the average gap between the electron levels

$$\Delta_m \approx \frac{E_F}{N},$$

the discreteness of which could, at the first glance, account for the modulation. For the particles studied, the modulation frequencies and the widths of energy gaps between the levels differ by an order of magnitude. Therefore, it was suggested²⁷⁵ that these modulations are due to vibrations of the particles. Analysis shows²⁷⁶ that the frequency of the acoustic vibrations of particles is close to the observed modulation frequency of the electron relaxation. The observed changes in the modulation frequencies and acoustic vibrations, depending on the particle size, are also consistent with experimental results.

Acoustic vibrations show themselves in the optical absorption spectra in the following way.²⁷⁵ In conformity with the Mie theory,¹⁹⁶ the absorption coefficient of a particle is

$$\kappa(\omega) \propto \varepsilon_m^{3/2} \frac{\omega \varepsilon_2(\omega)}{[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + \varepsilon_2(\omega)^2}. \quad (56)$$

The resonance absorption takes place when

$$\varepsilon_1(\omega) = -2\varepsilon_m.$$

In the free electron model,

$$\varepsilon_1(\omega) = 1 - \frac{\omega_0^2}{\omega^2 + \Gamma_e^2}, \quad \varepsilon_2(\omega) = \frac{\omega_0^2 \Gamma_e}{\omega(\omega^2 + \Gamma_e^2)}, \quad (57)$$

where Γ_e is the reciprocal relaxation time of electrons.

It can be seen from relations (52) and (57) that the position of the plasmon resonance depends on the density of electrons in the particle (because of a similar dependence of ω_0). As the electron density increases, the resonance shifts to shorter wavelengths; when the density decreases, it shifts to longer wavelengths. The possibility of this change in the position of the plasmon band was shown in experiments on pulse radiolysis²²⁷ of identical silver particles with a size of 6 nm. As a result of vibrations of the ionic lattice, the electron density in the particles changes periodically, which shows itself as the periodic modulation of absorption.

In a study of electron relaxation in experiments similar to those described above,^{266, 277} silver particles 40–60 nm in diameter and gold particles 15–20 nm in diameter were found to be broken to give smaller fragments (5–20 and 5 nm, respectively).

The fragmentation was induced by the radiation from a pumping laser able to cause ionisation of the particles. The radiation power played a minor role. The fragmentation was due to the appearance of an electric charge on the particles upon photoemission.²⁶⁶ This is confirmed by the fact that this effect was especially pronounced when the solution contained molecular traps for electrons.

VIII. Electron transfer through nanoparticles

Metal nanoparticles are unique objects to study the transfer of electrons through point contacts. For contacts between particles, non-linear current–voltage characteristics and (for low voltages) current suppression have been found.^{278–282} In recent years, nanoparticles have started to be used in experiments with point contacts. The tip of a tunnelling microscope normally serves as one of the electrodes in these experiments (Fig. 9).^{283–289} The intensive research along this line started after a single nanoparticle had been isolated and stabilised on a substrate.²⁷

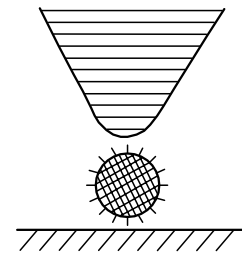


Figure 9. Scheme of the experiment on electron tunnelling through individual particles.

The observed anomalies of current–voltage characteristics were attributed from the beginning²⁷⁸ to the fact that an electron which skips from a particle to an electrode changes the particle charge by the magnitude of the electron charge e and thus increases the electrostatic energy by

$$\Delta E \approx \frac{e^2}{C},$$

where C is the capacitance of the particle. The capacitance of a spherical particle with the radius R coated by a shell with thickness d and having the dielectric constant ε in an electrolyte solution is found from the relation

$$C = 4\pi\varepsilon \frac{R}{d} (R + d).$$

For an electron to be able to skip (tunnel) from the particle to an electrode, the energy of the electron should be greater than ΔE . To ensure that the electron has the required energy, a relatively high voltage should be applied on the electrodes

$$U \approx \frac{e}{C}.$$

In experiments with single nanoparticles,^{27, 289} several steps can be found in the current–voltage characteristics (Fig. 10, curve 1). It was shown²⁸² that in the intervals between the steps, the particle charge does not change and is equal to e , $2e$, $3e$, etc. In addition, the conductivity of the electrode–particle system exhibits several maxima arranged at intervals (Fig. 11).

The maxima are due to degeneration of the electrostatic energy of the particle²⁹⁰

$$E(Q) = \frac{Q^2}{2C} + VQ \quad (58)$$

with respect to the charge Q ; here V is the potential of the particle. The condition of the energy degeneration with respect to charge

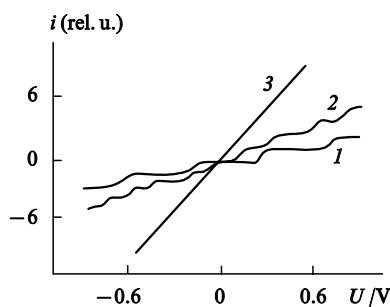


Figure 10. Current–voltage characteristics of a nanoparticle–electrode system for particles of different sizes increasing in the sequence $1 < 2 < 3$.

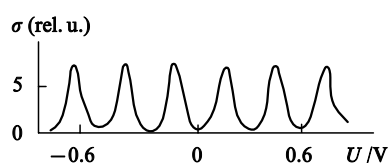


Figure 11. Electrical conductivity of a nanoparticle–electrode system vs. applied voltage.

$$E[(n-1)e] = E(ne)$$

is fulfilled for the potential

$$V_n = -\frac{(2n-1)e}{2C}. \quad (59)$$

The effects of tunnelling through single particles have been studied fairly comprehensively by electrochemical methods.²⁸⁷ Particles of different sizes were considered; in addition to experimental studies, data of numerical modelling of the processes occurring in the system shown in Fig. 9 were presented. In particular, transfer of electrons through the adlayer of the particles characterised by a particular size distribution was studied. It was shown that in the case of a particle ensemble of this type, the steps on the current–voltage characteristics are blurred and disappear with an increase in the particle size (see Fig. 10).

IX. Self-assembly of nanoparticles

Metal nanoparticles meant for the use as elements of electronic devices should finally be deposited on substrates. The properties of ensembles of deposited particles depend appreciably on their distribution over the substrate; this problem has drawn considerable attention. The possibility of deposition of ordered structures consisting of nanoparticles is of special interest; they can serve as miniature electronic devices: memory elements, lasers, screens, switches, *etc.* These ordered structures have been called quantum dots.^{291–293}

The periodic structures based on nanoparticles were initially prepared by deposition of atoms on specially prepared substrates. For example, a procedure for the preparation of ordered islands of silver on the Pt(III) surface has been described.²⁹⁴ The islands were formed as a result of nucleation of silver atoms on a substrate surface with a pre-formed structure of separate silver atoms. It is clear, however, that this procedure is applicable only to a very narrow range of materials; therefore, the search for new, more versatile methods for the preparation of ordered structures from nanoparticles continues. A possible approach is deposition of clusters grown beforehand.

The method of targeted deposition of clusters was apparently implemented for the first time by Fucks *et al.*²⁹⁵ Low-energy monodisperse clusters obtained from the gas phase were deposited *in vacuo* on a substrate. Cluster sub-monolayers containing several

tens to several thousands of atoms were prepared in this way. Observations showed that these clusters are not destroyed when brought in contact with a solid support. For big clusters, diffusion coefficients over the surface are low; therefore, the clusters do not migrate over the surface, their coalescence also being largely suppressed. As clusters are accumulated on the substrate, peculiar structures corresponding to successive deposition of strongly fixed particles are formed.

The resulting films are highly porous and are formed from aggregates of nanoclusters having a fractal structure similar to that found for particles in thin polymeric films.^{237, 238} The fractal dimension and characteristic size of the aggregates are determined by the regime of cluster deposition on the substrate.

It has been proposed²⁹⁶ to deposit energy-charged clusters; in this case, characteristics of the structures formed can be varied over wider limits. The process of formation of structures from deposited clusters was also modelled in numerical experiments. Experimental data and the results of modelling have been surveyed in reviews.^{297, 298}

Ordered structures consisting of nanoparticles supported on substrates are of the greatest interest. These structures were first obtained using self-assembled monolayers of surfactants and resorting to the lithography methods. It has been shown^{299–306} that deposition of surfactant monolayers followed by treating them with beams of low- or high-energy electrons or ultraviolet radiation and the use of scanning tunnelling microscopy affords ordered structured layers of metal particles with characteristic dimensions of up to 20 nm. Periodic structures of metal nanoparticles have also been prepared³⁰⁷ by deposition of a metal on a substrate coated by an ordered adlayer of inert particles with sizes from 50 nm to 30 nm. In this case, the metal is applied on the substrate through the spaces between the inert microparticles.

In recent years, considerable progress has been made in the development of a method that implies formation of ordered nanostructures (colloid crystals) directly from nanoparticles formed in colloidal solutions. The attraction of this method is that it provides the possibility of varying the particle size over wide limits, the structure of the particles being controlled quite reliably by advanced techniques. In addition, the ligand or adsorption shell and, hence, the electronic properties of the particles can be varied as desired. Finally, successful use of this method hardly depends on the nature of the particles.

A method for the preparation of colloid crystals was first realised for CdS nanoparticles.³⁰⁸ The procedure of evaporation of a solution from a colloidal dispersion film was used. During evaporation, either homogeneous or heterogeneous (on the substrate) nucleation of colloid crystals takes place. By this method, one can form both three- and two-dimensional colloid crystals. The scheme of deposition of ordered nanostructures is presented in Fig. 12. The resulting structures were studied by electron microscopy, which showed the presence of nanocrystals with ordering in the range of about 50 μm.

Subsequently, this method has been widely used to prepare ordered structures from metal nanoparticles.^{31, 48, 309–319} Initially, the experiments were carried out with gold nanoparticles because in this case, the composition of the particles was constant and the

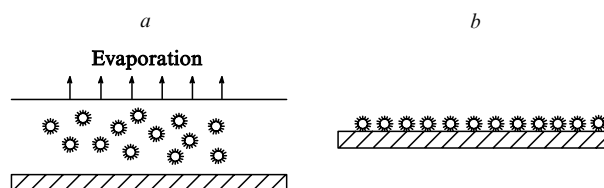


Figure 12. Scheme of the formation of ordered structures from nanoparticles by evaporation of the solvent. System: (a) before evaporation; (b) after evaporation.

ligand shell formed from alkanethiols was sufficiently stable to ensure high stability of the colloidal dispersion and a colloid crystal. In addition, gold nanoparticles coated by an alkanethiol adlayer permit easy replacement of the solvent; the nanoparticles can be deposited and again dispersed and exchange reactions with the ligand environment can be carried out.

It has been demonstrated in various studies that nanoparticles form either a planar hexagonal structure or crystals with an FCC lattice. Detailed investigations dealing with the structure of colloid crystals and its dependence on the structure of nanoparticles have been carried out.^{19, 20, 320} It was found that in the case of ordered multilayer structures, a colloid crystal necessarily has the (111) face. This was explained by the important role of the surface forces in the formation of colloid crystals because in ordinary crystals, this face has the minimum surface energy.

The lattice of a colloid crystal formed by gold nanoparticles and stabilised by quaternary ammonium bromides with alkyl radicals of various lengths has been studied.³¹⁹ It was found that the lattice parameter of the colloid crystal depends linearly on the length of the hydrocarbon radical. When the second layer of nanoparticles is deposited, they form either linear or ring structures on the hexagonal lattice formed by the first layer. The particles in the second layer occupy preferentially the sites above the contact points of the first-layer particles.

Characteristic features of the packing of particles have also been studied for the colloid crystals of gold²⁰⁰ and silver³²¹ stabilised by alkanethiols. In this case, too, a correlation was established between the length of the alkyl chain and the lattice parameter of the colloid crystal. In addition, it was found by the method of chemical imaging in transmission electron microscopy with electron energy filtering³²¹ that the alkyl 'tails' of the adlayer of one particle penetrate rather deeply into the adlayers of neighbouring particles and form a sort of chemical bond with them. These experimental data confirm the results of molecular dynamics modelling of the behaviour of long-chain alkanethiols on the surface of nanocrystals.³²²

The interaction between silver nanoparticles coated by thiolates and forming ordered structures has been studied in detail.³²³ The aggregation of nanoparticles and the structural transitions in thin layers and in the bulk of the colloidal solution were investigated. By comparing the experimental data with the results of numerical modelling, parameters of the particle–particle interaction were determined for the van der Waals attraction and for the short-range repulsion. It was shown that model of 'soft spheres' is the most adequate model for nanoparticles. A more comprehensive theoretical study of the characteristic features of nanoparticle structuration at interfaces has been carried out by Gelbart *et al.*³²⁴

For the preparation of colloid crystals by vaporisation, the monodispersity and the shape of particles and the nature of the stabilising shell are significant. Self-assembly of gold, silver and platinum nanoparticles has been studied.⁵¹ Nanoparticles were first prepared in water and then transferred into organic solvents containing thiolates; thus, the particle size and shape could be varied over wide limits. All the systems studied displayed the capability of self-assembly. The effect of the stabilising agent on the preparation of colloid crystals from nanoparticles has been considered by Lin *et al.*,³²⁵ who worked with gold nanoparticles synthesised in reverse micelles using various stabilisers containing thiol, amino and sulfide groups. It was found that the formation of colloid crystals proceeds most readily in the presence of ligands with thiolate groups. The use of dodecanethiol was found to be the most efficient; with this compound, colloid crystals are spontaneously formed, nanoparticles being spontaneously segregated according to their sizes.

Nanoparticles arranged in crystals exhibit new cooperative properties;^{46, 326} in particular, for two-dimensional crystals, the plasmon band shifts towards lower energies with respect to that for isolated nanoparticles. This effect is more pronounced when three-dimensional colloid crystals are formed; in this case the

profile of the absorption band also changes. This change in the band profile is due to the influence of the particle environment and to the tunnelling of electrons between them. The latter factor starts to be significant when the distances between the particles are close to 2 nm; the average distance between nanoparticles coated by, *e.g.*, dodecanethiol is 1.8 nm.

The hypothesis concerning the influence of tunnelling on the absorption spectra has been verified;³²⁷ for this purpose, the energy shift of the plasmon band and the coefficient of light reflection from self-assembled structures consisting of silver particles with various distances between the closest particles were studied. Experimental data were approximated by theoretical curves constructed using the Maxwell–Garnett model. As particles approach one another to distances of several nanometers, the optical characteristics change sharply and the discrepancy between the calculated and experimental data becomes more pronounced. A substantial deviation of the results obtained in terms of classical theory from experimental results was found for the non-linear susceptibility of nanoparticle crystals, which characterises the generation of the second optical harmonics.

The cooperative effects in self-assembled nanoparticles are so pronounced that it is possible to obtain structures exhibiting dichroism by special techniques.³²⁸ It is even possible to control the optical characteristics of ordered layers of nanoparticles.⁴² The relevant experiments were concerned with the regularities of light transmission through and light reflection from multilayer films consisting of isolated gold nanoparticles. The experiments were carried out under conditions where a potential was applied on the film (by injection of electrons). Both the reflectance and the transmittance changed upon application of the potential. It was found that the observed changes in the optical constants cannot be described in terms of the views on the individual behaviour of nanoparticles.

To promote self-assembly of nanoparticles into a supported crystal, special methods are used, for example, pre-treatment of the substrate,³²⁹ which can consist in the preliminary formation of self-assembled monolayers (Fig. 13) the external part of which reacts efficiently with the particles or with their ligand environment; in this case, the nanoparticles are stabilised by complex surfactants having two functional groups selected according to the 'key–lock' principle (Fig. 14).

Langmuir–Blodgett films^{46, 333} and electrophoretic deposition of nanoparticles^{334, 335} have been used to design ordered structures of nanoparticles. Ordered structures of silver nanoparticles have also been prepared by thermal reduction of the

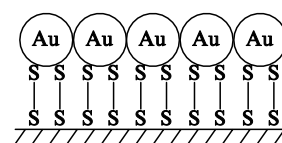


Figure 13. Scheme of the formation of ordered structures from nanoparticles on self-assembled monolayers.³³⁰

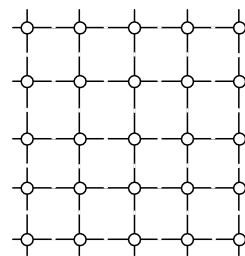


Figure 14. Scheme of the design of ordered structures from nanoparticles modified by surfactant vapours selected according to the 'key–lock' principle.^{331, 332}

metal in a solution applied onto the surface of specially pre-treated mesoporous silica.³²⁹ By using block copolymers which allow microphase separation, an ordered distribution of particles in films³³⁶ and the formation of intricate structures from nanoparticles³³⁷ can be attained. These structures can rearrange upon thermal treatment or upon introduction of additives influencing the microphase state of the block copolymer. Ordering of nanoparticles on a molten surface of a polymer the bulk phase of which remains solid has also been observed.³³⁸

Recent years have been marked by vigorous development of the methods for the preparation of self-assembled structures from nanoparticles with the use of biological objects: lipid tubes³³⁹ or oligodesoxyribonucleotides containing terminal thiol groups,^{340–342} which act as efficient organising agents in the case of gold nanoparticles. Biological systems permit several types of self-assembly of nanoparticles;³⁴³ for example, the method found to be efficient for gold nanoparticles includes the use of streptavidin and biotin analogues. Biotin disulfide can be adsorbed on gold nanoparticles, which is followed by introduction of streptavidin; otherwise, biotin disulfide is bound to streptavidin and the complex is then adsorbed on the particles introduced. The complexity of this procedure is justified by the presence of a large number of biotin and streptavidin analogues and by the possibility of controlling the structure of the nanoaggregates synthesised and of preparing ordered structures of nanoparticles directly in solution.

X. Conclusion

The high practical value of nano-sized colloidal systems has stimulated substantial progress in their investigation in the last decade. Modern experimental equipment has enabled the preparation of individual nanoparticles with a specified size and the investigation of their properties. The advances in the synthesis and in the study of nanoparticles confirmed the theoretical models that had been developed decades ago but could not be verified because they were developed for ideal systems. It can be said that the high level achieved in the experiments on the preparation of nanoparticles is now close to the reachable limit. The methods used to investigate the properties of nanoparticles have also substantially improved. Almost exhaustive information on the structures of nanoparticles and on the electron dynamics in them was obtained. All this ensured transition to a new level of understanding of the physicochemical processes taking place in nano-sized colloidal systems.

However, the progress brought out new problems. The crucial role of the surface in the formation of properties of nanoparticles has become obvious. Nevertheless, the possibility of preparing nanoparticles with specified surface characteristics are still limited. The influence of the environment on the properties of nano-sized systems has not been adequately elucidated. There appeared the necessity of the development of theoretical approaches to the description of the properties of nanoparticles with intermediate sizes for which cooperative dynamics of electrons is replaced by the individual dynamics. New theoretical models describing the cooperative effects in nanoparticle ensembles including those taking into account the cooperation of their electronic component are required. At present, there are even no models which take into account the influence of the ligand (adsorption) shells when considering the dynamics of electrons in nanoparticles. In this respect, experimental research goes markedly ahead of the theory. However, experimental data now available constitute a good basis for the development of a more comprehensive theory of nanoparticle ensembles.

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^c — *Russ. J. Phys. Chem. (Engl. Transl.)*

^d — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*

^e — *Russ. Chem. Bull. (Engl. Transl.)*

^f — *Polym. Sci. (Engl. Transl.)*

Heterocyclisation of trisubstituted formamidines containing an aryl or hetaryl substituent at the imine nitrogen atom

G V Oshovsky, A M Pinchuk

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Abstract. Published data on the cyclisation of N^1, N^1 -disubstituted N^2 -aryl- and N^2 -hetaryl-formamidines are analysed, described systematically and generalised. The bibliography includes 147 references.

I. Introduction

Heterocyclisations play an important role in organic chemistry and provide key, sometimes irreplaceable, approaches to the preparation of heterocyclic systems. Since heterocyclic derivatives represent the most numerous class of organic compounds covering about two-thirds of all natural and synthetic products, it is important to describe systematically the methods used to prepare them. At present, the syntheses of heterocyclic compounds are classified using three different approaches: in terms of the cyclisation product (heterocyclic compound or a class of compounds), in terms of the type of ring-forming reaction, and in terms of the functional groups or classes of organic compounds involved in the construction of the heterocycle. The last-mentioned approach attracts special attention because it discloses the synthetic potential and the advantages and disadvantages of heterocyclisation components and represents more vividly the methods suitable for solving sophisticated synthetic problems.

Amidines are important starting compounds in the synthesis of heterocyclic systems of various types. There are several ways of construction of heterocycles with participation of amidines

(a) cyclisation upon the reaction with the NH group of the amidine;

(b) transformation of the reactive CH groups attached to the amidine carbon atoms;

(c) pericyclic reactions;

(d) reaction of the electrophilic amidine carbon atoms with external or internal nucleophiles.

Only routes (a) and (b) have been considered comprehensively in the literature.^{1–5} In this review, we analyse the prospects for using N^1, N^1 -disubstituted N^2 -aryl- and N^2 -hetarylformamidines (hereinafter, referred to as aryl- and hetarylformamidines, respectively) for the construction of simple and fused heterocycles. These

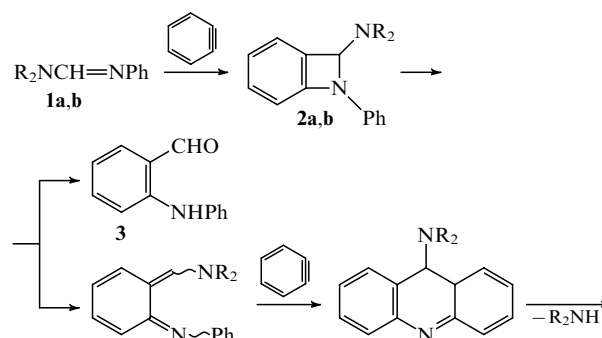
compounds cannot react by routes (a) and (b); therefore, it becomes possible to focus attention on the key reactions of types (c) and (d) and to extend the existing generalisations and views on the role of amidines in the synthesis of heterocyclic systems.

II. Pericyclic and cyclisation reactions initiated by nucleophilic addition to multiple bonds

1. Cycloaddition

N^1, N^1 -Dimethyl- N^2 -arylformamidines and N^1, N^1 -dimethyl- N^2 -hetarylformamidines can play a dual role in cycloaddition: they either provide the imine fragment of the dimethylaminomethylideneamino group $N=CHNMe_2$ (hereinafter, the amidine fragment) for heterocyclisation or act as heterodienes in which the amidine fragment $N=CH$ is conjugated with the double bond of the substituent at the imine nitrogen atom. The latter pathway is realised only for N -hetarylamidines characterised by a high degree of alternation of single and double bonds. In these compounds, the double bond in a heterocyclic substituent is activated by the electron-donating amidine group;⁶ hence, the Michael addition to this bond is possible. The primary reaction products can cyclise to give compounds with the same structure as those formed upon concerted [2+4]-cycloaddition. In these products, recyclisation of heterocyclic fragments is possible, resulting in new heterocyclic compounds.

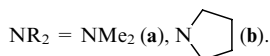
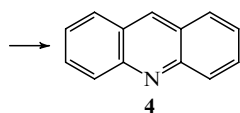
N^1, N^1 -Dimethyl- N^2 -phenylformamide **1a** and phenyliminopyrrolidinomethane **1b** react with dehydrobenzene according to the [2+2]-cycloaddition pattern⁷ giving rise to unstable benza-zetines **2a,b**, which are converted into 2-phenylaminobenzaldehyde **3** and acridine **4** under the reaction conditions.



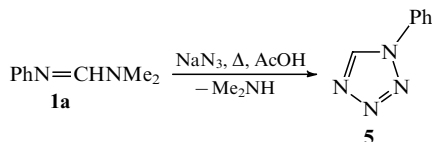
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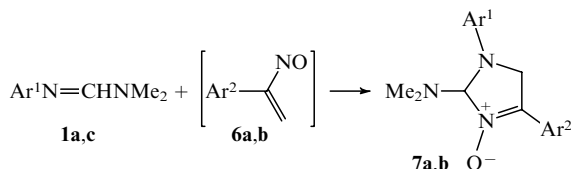
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The amidine **1a** reacts with sodium azide according to the [2 + 3]-cycloaddition route to give ⁸ 1-phenyltetrazole **5**.

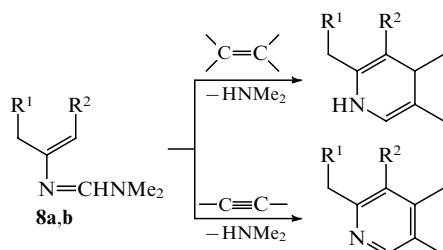


1-Nitrosovinylaryls **6a,b**, generated *in situ* from halooximes, react with *N*¹,*N*¹-dimethyl-*N*²-arylformamidines **1a,c** according to the [3 + 2]-cycloaddition route to give 1,4-diaryl-2-dimethyl-amino-3-oxy-2,5-dihydro-1*H*-imidazoles **7a,b**.^{9,10}



Ar¹ = Ar² = Ph (**1a**, **6a**, **7a**), 4-MeC₆H₄ (**1c**, **6b**, **7b**).

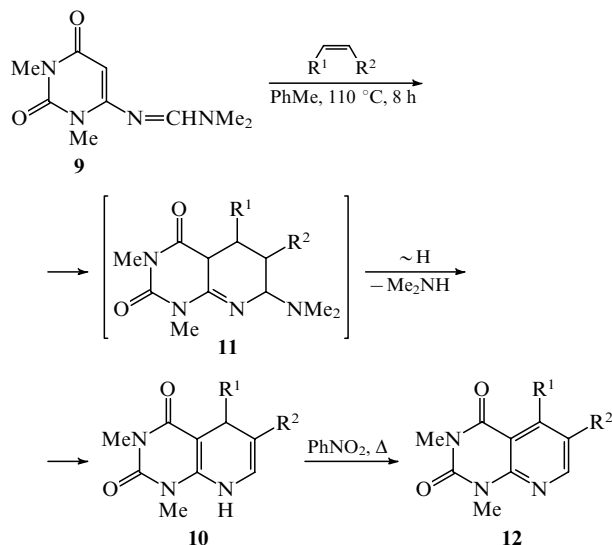
In the case of *N*¹,*N*¹-dimethyl-*N*²-hetarylformamidines containing many alternating single and double bonds, heterocyclisation involves the azomethine fragment of the amidine substituent and the neighbouring vinylene fragment of the heterocycle. The diene reactivity increases in the sequence *N*¹,*N*¹-dimethyl-*N*²-arylformamidines, *N*¹,*N*¹-dimethyl-*N*²-hetarylformamidines and *N*¹,*N*¹-dimethyl-*N*²-vinylformamidines. This is determined by the degree of participation of the vinylene fragment in conjugation. Indeed, *N*¹,*N*¹-dimethyl-*N*²-phenylformamidines derivatives do not participate in cycloaddition reactions as dienes, whereas *N*¹,*N*¹-dimethyl-*N*²-vinylformamidines are quite reactive dienes. On passing from *N*-vinylformamidines to *N*-hetarylformamidines, the diene reactivity decreases. *N*¹,*N*¹-Dimethyl-*N*²-(isopropenyl)formamidine **8a** and *N*¹,*N*¹-dimethyl-*N*²-(cyclohex-1-enyl)formamidine **8b** readily react with alkenes and alkynes¹¹ to give 1,4-dihydropyridine and pyridine derivatives formed as [4 + 2]-cycloaddition products.



R¹ = R² = H (**a**); R¹ - R² = (CH₂)₃ (**b**).

The reactions of *N*¹,*N*¹-dimethyl-*N*²-(1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-yl)formamidine **9** with methyl vinyl ketone, methyl acrylate, acrylonitrile and dimethyl or diethyl maleate proceed in a similar way to give 1,3-dimethyl-5,8-dihydropyrido[2,3-*d*]pyrimidine-2,4-diones **10**, which are formed from the products of primary [2 + 4]-cycloaddition **11**.¹² The high regioselectivity observed in the reactions with mono-substituted alkenes is in line with the electron-donating influence of the amidine substituent, which increases the electron density at the 5-position of amidinodimethyluracil **9**. The compounds **10**

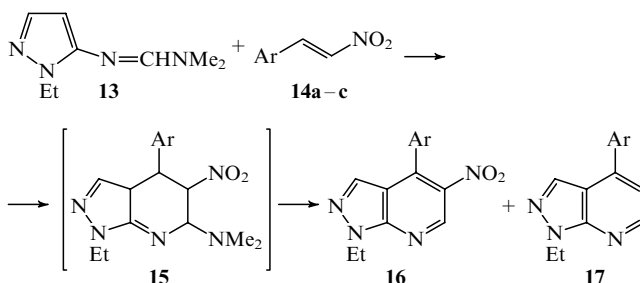
were oxidised to the corresponding 1,3-dimethylpyrido[2,3-*d*]pyrimidine-2,4-diones **12** by refluxing in nitrobenzene.



R¹ = H; R² = COMe, CO₂Me, CN; R¹ = R² = CO₂Et, CO₂Me.

*N*¹,*N*¹-Dimethyl-*N*²-5-(1-ethylpyrazolyl)formamidine **13** undergoes [2 + 4]-cycloaddition to (2-nitrovinyl)benzene **14a**, 1-phenyl-3-(2-nitrovinyl)indole **14b** or 2-(2-nitrovinyl)thiophene **14c** on exposure to microwave radiation.¹³ The adducts **15** formed regioselectively are converted *in situ* into a mixture of 4-aryl-1-ethyl-5-nitropyrazolo[3,4-*b*]pyridines **16** and 4-aryl-1-ethylpyrazolo[3,4-*b*]pyridines **17** as a result of abstraction of HNO₂ with aromatisation.

The ratio of the compounds **16** and **17** depends on the nature of the nitroalkene **14** but the nitro derivative **16** predominates in all cases.

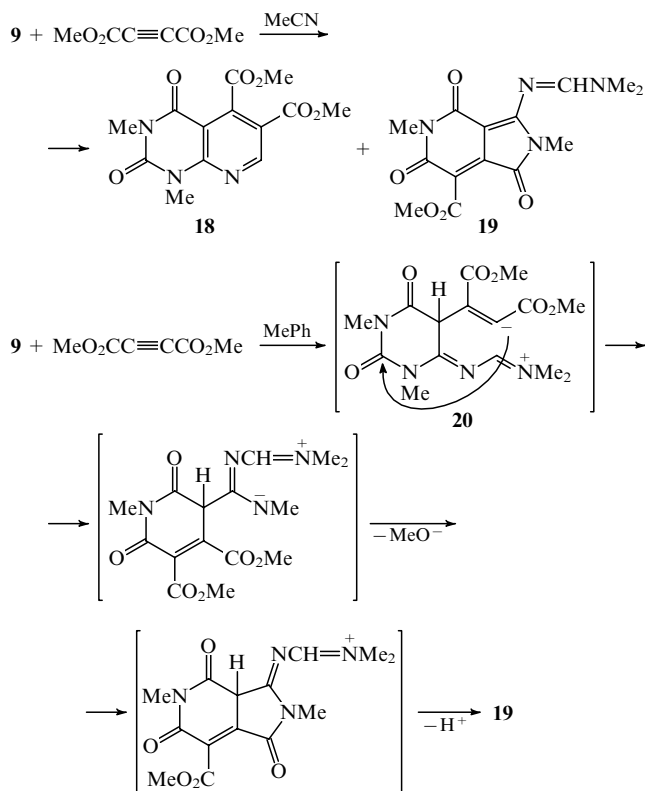


Nitroalkene 14	Ar	Yield (%)	
		16	17
a	Ph	64	8
b		60	9
c		84	—

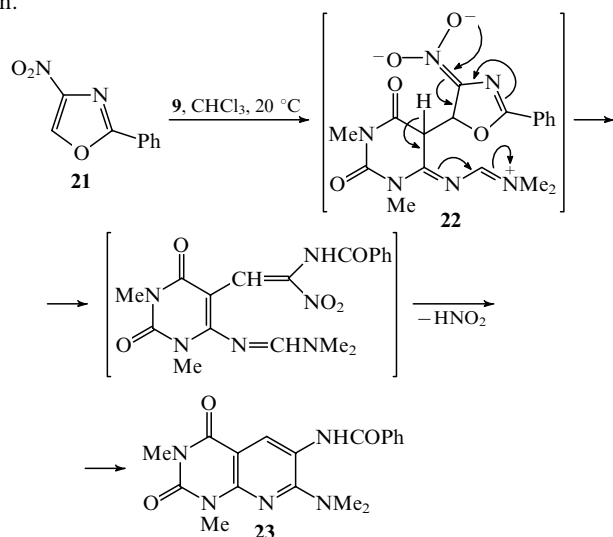
2. Recycling

In the reactions of heterocyclic derivatives of amidines with activated alkynes, Michael addition is the preferred reaction route, as opposed to the reactions of *N*-vinylformamidines. Indeed, the reaction of the compound **9** with dimethyl acetylenedicarboxylate in acetonitrile (20 °C, 36 h) affords a mixture of dimethyl 1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrido[2,3-*d*]pyrimidine-5,6-dicarboxylate **18** and methyl 2,5-dimethyl-3-(3-methyl-1,3-diazabut-1-enyl)-1,4,6-trioxo-2,4,5,6-tetrahydropyrrolo-[3,4-*c*]pyridine-7-carboxylate **19** in 1 : 2 ratio. The reaction carried out in toluene (16 h) or chloroform (18 h) gives only the compound **19** in

70% yield. It was suggested¹⁴ that this compound results from recyclisation of the uracil residue in the Michael addition product **20** formed initially.



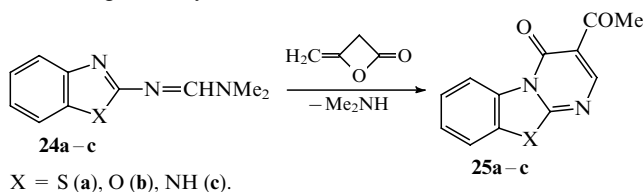
A reactive dienophile, 4-nitro-2-phenyloxazole **21**, reacts with amidinouracil **9** according to the Michael addition pathway, although its reactions with other dienes follow the [2 + 4]-cycloaddition route.¹⁵ The intermediate **22** is converted into 6-benzamido-7-dimethylamino-1,3-dimethyl-2,4-dioxo-1,2,3,4-tetrahydropyrido[2,3-*d*]pyrimidine **23** through opening of the oxazole ring followed by an electrocyclic reaction accompanied by aromatisation.



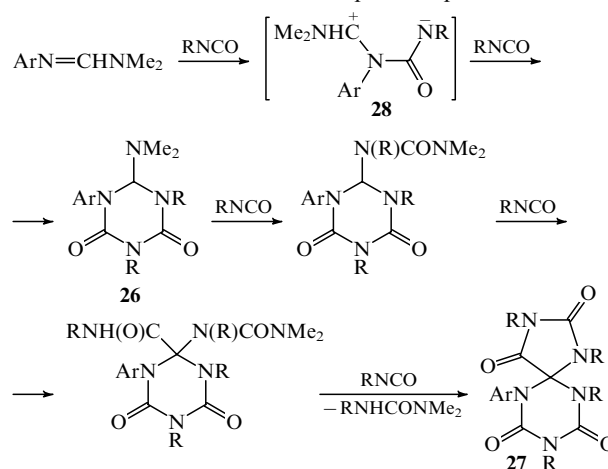
3. Reactions with diketene and isocyanates

The reactions of *N*-hetarylformamidines with diketene have been studied in relation to systems containing a pyridine nitrogen atom at the α -position relative to the amidine substituent, namely, *N*¹,*N*¹-dimethyl-*N*²-benzothiazol-2-ylformamidine **24a**, *N*¹,*N*¹-dimethyl-*N*²-benzoxazol-2-ylformamidine **24b** and *N*¹,*N*¹-dimethyl-*N*²-benzimidazol-2-ylformamidine **24c**. These reactions

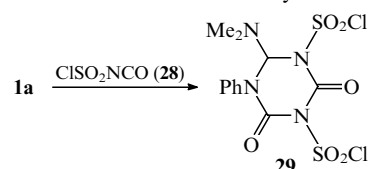
proved convenient for the construction of fused pyrimidine-containing heterocycles **25a–c**.^{16, 17}



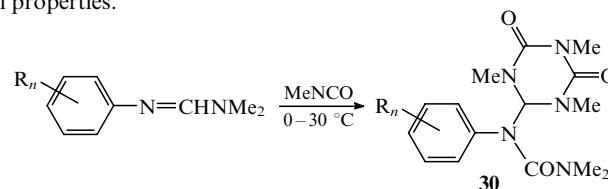
In the general case, *N*¹,*N*¹-dimethyl-*N*²-arylformamidines react with aryl isocyanates to give 1:2 adducts, 1,3,5-triazines **26**.^{18, 19} However, apart from these products, the reactions afford solid substances with high melting points, which have been identified^{20–22} as 1,3,6,8,10-pentaazaspiro[4.5]decane-2,4,7,9-tetraones **27**. Presumably,^{20, 22} they are formed *via* bipolar intermediate **28**, which regioselectively adds isocyanate giving rise to *sym*-triazinedione **26**. Successive insertion of isocyanate into the C–N and C–H bonds results in the spiro compound **27**.



4-Dimethylamino-2,6-dioxo-5-phenyl-4,5-dihydro-1,3,5-triazine-1,3-disulfonyl dichloride **29** is produced in the reaction of the amidine **1a** with Graf's isocyanate **28**.²³



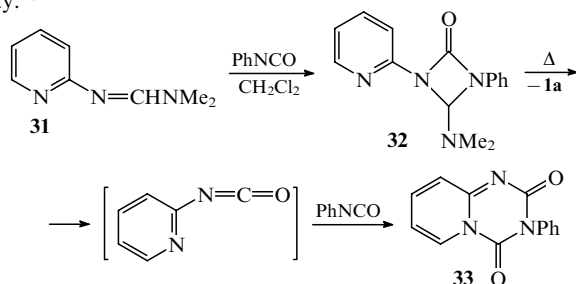
An unusual cycloaddition of methyl isocyanate to *N*¹,*N*¹-dimethyl-*N*²-arylformamidines has been proposed²⁴ as a method for the synthesis of 3-aryl-1,1-dimethyl-3-(1,3,5-trimethyl-4,6-dioxo-1,2-dihydro-1,3,5-triazin-2-yl)ureas **30**, possessing herbicidal properties.



$R_n = \text{H, Cl, Cl}_2, 3\text{-CF}_3, 4\text{-MeO, 4-Me, 3-Cl-4-MeO, 3-Cl-4-Me, 3-CF}_3\text{-4-Cl.}$

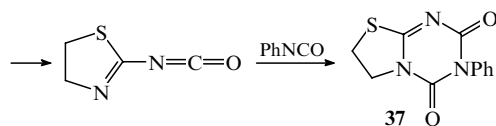
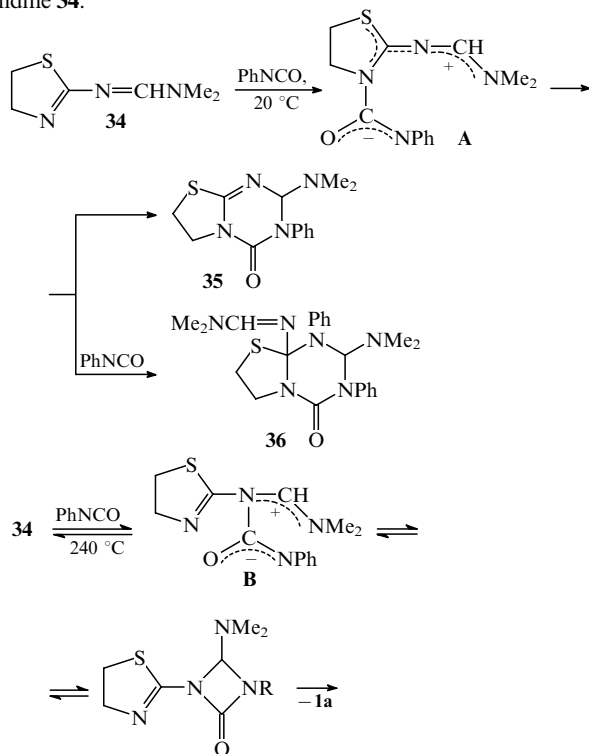
Some reactions of *N*-hetarylformamidines with isocyanates differ from the transformations of *N*-arylamidines because either heteroatoms or activated multiple bonds of the heterocycle are involved in the reaction. Thus the reaction of *N*¹,*N*¹-dimethyl-*N*²-2-pyridylformamidines **31** with phenyl isocyanate gave a [2 + 2]-cycloadduct, 4-dimethylamino-1-phenyl-3-pyridin-2-yl-1,3-diazetidin-2-one **32**, in a high yield. At elevated temperature in the presence of phenyl isocyanate, this product is converted into

3-phenylpyrido[1,2-*a*]-1,3,5-triazine-2,4-dione **33**.²⁵ 3-Phenylpyridazino[1,6-*a*]-1,3,5-triazine-2,4-dione is prepared in a similar way.²⁶



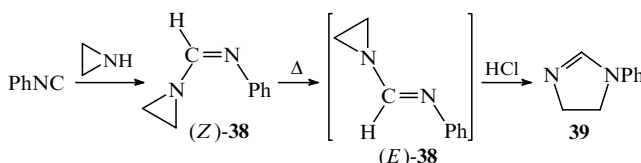
Presumably,²⁵ the cycloadduct **32** formed initially undergoes cyclodegradation at elevated temperatures. The subsequent [2 + 4]-cycloaddition of the resulting isocyanates gives rise to the bicyclic adduct **33**.

Depending on the temperature and the reactant ratio, the reactions of *N*¹,*N*¹-dimethyl-*N*²-2-(4,5-dihydrothiazol-2-yl)formamides **34** with phenyl isocyanate afford different products, 2-dimethylamino-3-phenyl-2,3,6,7-tetrahydrothiazolo[3,2-*a*]-1,3,5-triazin-4-one **35**, *N*¹,*N*-dimethyl-*N*²-(2-dimethylamino-4-oxo-1,3-diphenylhexahydrothiazolo[3,2-*a*]-1,3,5-triazin-8*a*-yl)formamidine **36** or 3-phenyl-6,7-dihydrothiazolo[3,2-*a*]-1,3,5-triazine-2,4-dione **37**.²⁷ In the opinion of the researchers cited, phenyl isocyanate reacts with the endocyclic imine nitrogen atom of the hetarylamidine **34** at room temperature; this gives rise to intermediate bipolar compound **A**. This compound either cyclises to yield compound **35** or reacts with a second phenyl isocyanate molecule, resulting in the amidine **36**. At elevated temperatures, the attack by phenyl isocyanate on the exocyclic imine nitrogen atom of the amidine **34** proves to be the preferred reaction pathway; this gives initially intermediate **B**, which is converted into compound **37** upon the reaction with phenyl isocyanate. Apparently, an important stage of this transformation in the latter case is transamination, *i.e.* the exchange by the imine fragments between phenyl isocyanate and the amidine **34**.



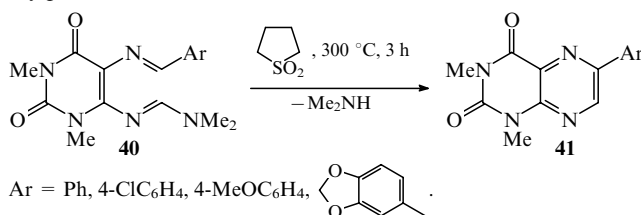
4. Electrocyclic reactions

The transformation of phenyliminoaziridinomethane **38** into 1-phenyl-4,5-dihydro-1*H*-imidazoline **39** induced by nucleophiles or acids proceeds similarly to the symmetry-allowed synchronous isomerisation of vinylcyclopropane into cyclopentene. The rearrangement is similar to the isomerization of vinyl ethyleneimine into pyrroline. The researchers suggested^{28,29} that the reaction of aziridine with phenyl isocyanide gives rise to thermodynamically unstable *Z*-isomer **38**, the transformation of which into the imidazoline **39** proceeds *via* initial *Z,E*-isomerization.

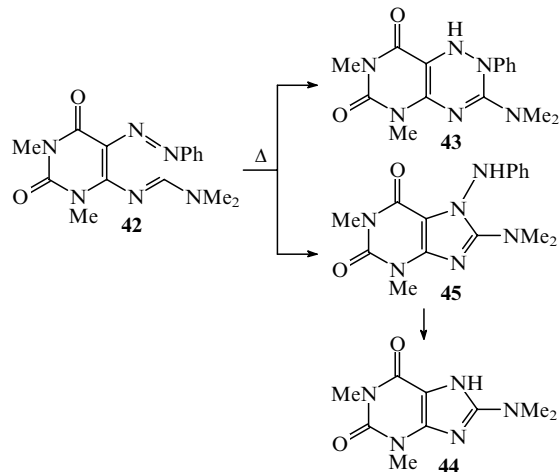


On heating or irradiation, *N*-hetarylamidines containing a substituent with an unsaturated fragment in the neighbouring position to the amidine group undergo sigmatropic transformations giving rise to more complicated heterocyclic systems.

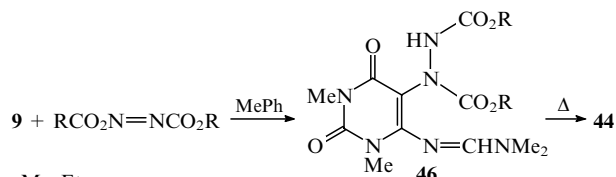
Thermolysis of *N*¹,*N*¹-dimethyl-*N*²-6-(5-arylideneamino-1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-yl)formamidine **40** is accompanied by the aza Cope reaction. An intramolecular pericyclic reaction followed by isomerisation and elimination of dimethylamine affords 6-substituted 1,3-dimethylpteridine-2,4-dione **41**.³⁰



Transformations of this type are also typical of systems containing an azo fragment in the neighbouring position to the amidine substituent, although they are accompanied by side processes. Thus *N*¹,*N*¹-dimethyl-*N*²-6-(1,3-dimethyl-2,6-dioxo-5-phenylazo-1,2,3,6-tetrahydropyrimidin-4-yl)formamidine **42** is converted at 210–220 °C into a mixture of 3-dimethylamino-5,7-dimethyl-2-phenyl-1,5-dihydro-2*H*-pyrimido[4,5-*e*]-1,2,4-triazine-6,8-dione **43** and 8-dimethylamino-1,3-dimethylpyrine-2,6-dione **44**. Apparently, the latter product is formed from 9-anilino-8-dimethylamino-1,3-dimethylpurine-2,6-dione **45**.³¹

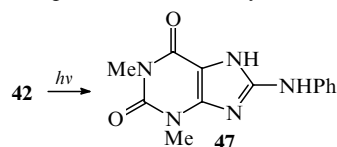


The reactions of amidinouracil **9** with azodicarboxylates proceed similarly to transformations of 6-amino- or 6-alkylamidinouracils to give adducts **46**. These products are converted into pyrine derivatives **44** upon thermal cyclisation.¹⁴

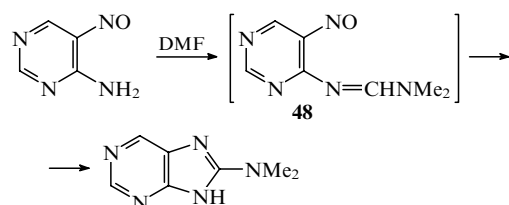


R = Me, Et.

In the photolysis of formamidine **42**, 1,5-cycloaddition is the predominant reaction pathway;^{32,33} 8-phenylamino-1,3-dimethylpurine-2,6-dione **47** is formed upon irradiation. A similar transformation takes place in the reductive heterocyclisation of the compound **42** induced by sodium dithionite.³⁴



The intramolecular 1,5-cycloaddition in *N*¹,*N*¹-dimethyl-*N*²-(5-nitrosopyrimidin-4-yl)formamidine **48** proceeds at room temperature without irradiation.³⁵



III. Intramolecular nucleophilic substitution

1. Reactions with participation of N-nucleophiles

*N*¹,*N*¹-Dimethyl-*N*²-arylformamidines and *N*¹,*N*¹-dimethyl-*N*²-hetarylformamidines are convenient objects for heterocyclisation, provided that a position adjacent to the amidine substituent is occupied by a reactive functional group (amino, carbonyl, ethoxycarbonyl, nitrile, iminophosphorane group and so on).

The reactions in which an N-nucleophile reacts with formamidine in the key stage of ring formation are summarised in Table 1. It should be emphasised that this approach is especially attractive for the synthesis of fused systems which include five-, six- and seven-membered nitrogen-containing heterocyclic fragments. The use of functionalised amidines in the synthesis of various fused pyrimidines has been studied most thoroughly.

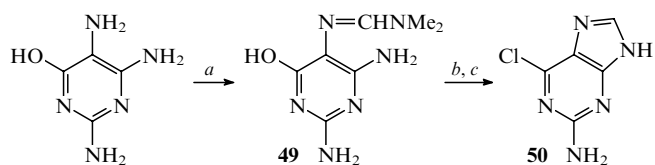
Cyclisation can either involve a nitrogen-containing nucleophile present in the molecule or occur upon the addition of ammonia, amines, hydroxylamine, their salts and hydrazine or guanidine. In some cases, the reaction is accompanied by deamination, *i.e.* transformation of the amidine substituent into an amino group.

Aryl- and hetarylformamidines containing a free amino group in the position neighbouring to the amidine substituent are postulated as intermediates in several syntheses of imidazoles from 1,2-diamines. Meanwhile, *N*²-(2,4-diamino-6-hydroxypyrimidin-5-yl)-*N*¹,*N*¹-dimethylformamidine **49** is a stable compound because the electron-donating substituents in the pyrimidine ring decrease the electrophilicity of the formamidine carbon atom.

Formamidines **49** can be converted into 2-amino-6-chloropurine **50** on treatment with HCl and subsequent heating.³⁶

Table 1. Products of heterocyclisation of aryl- and hetarylformamidines formed with participation of N-nucleophiles.

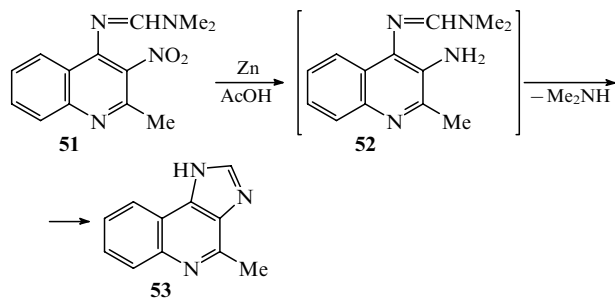
Type of reaction	X	Reagent or reaction conditions	Reaction product
<i>a</i>	NH ₂	Δ	
<i>b</i>	CH ₂ NHPh	Δ	
<i>c</i>	CH(R)CH ₂ NH ₂	Δ	
<i>d</i>	CN	RNH ₂	
<i>e</i>	CN	H ₂ NNH ₂	
<i>f</i>	CN	H ₂ NOH	
<i>g</i>	CN	(H ₂ N) ₂ C=NH	
<i>h</i>	C(O)R	NH ₃	
<i>i</i>	C(O)R ¹	R ² NH ₂	
<i>j</i>	CO ₂ Et	RNH ₂	
<i>k</i>	P ⁺ (Cl)(NR ₂) ₂ Cl ⁻	NH ₃	
<i>l</i>	CHO	NH ₂ OH	



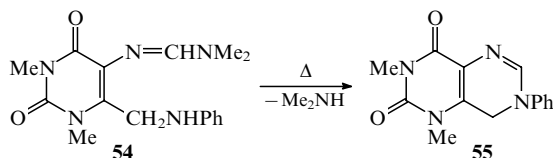
(a) POCl₃, DMF; (b) HCl, H₂O; (c) Δ, -Me₂NH·HCl.

Hetarylamidines containing a free amino group are synthesised by selective reduction of nitro- or cyano-substituted amidines. Under the reaction conditions, they undergo heterocyclisation according to route *a* (see Introduction) giving rise to an imidazole fragment. Thus reduction of *N*¹,*N*¹-dimethyl-*N*²-(2-methyl-3-nitroquinolin-4-yl)formamidine **51** results in *N*²-(3-amino-2-

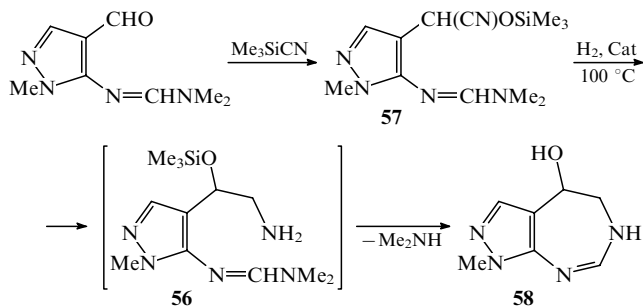
methylquinolin-4-yl)- N^1,N^1 -dimethylformamide **52**, which undergoes intramolecular cyclisation *in situ* to give 4-methylimidazo[4,5-*c*]quinoline **53**.³⁷



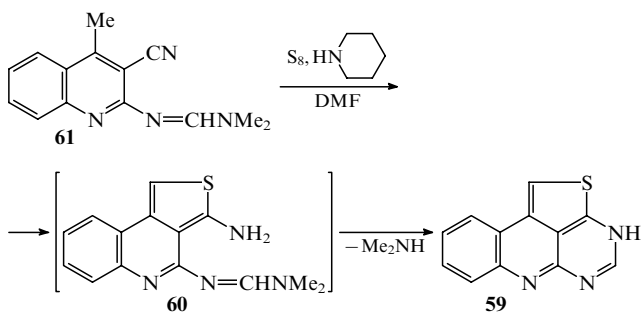
The electron-donating effect of the dimethyluracil moiety accounts for the stability of N^1,N^1 -dimethyl- N^2 -(1,3-dimethyl-2,4-dioxo-6-phenylaminomethyl-1,2,3,4-tetrahydropyrimidin-5-yl)formamide **54**; it is converted into 1,3-dimethyl-7-phenyl-7,8-dihydropyrimido[5,4-*d*]pyrimidine-2,4-dione **55** only on heating in toluene.³⁸



Cyclisation *in situ* of N^1,N^1 -dimethyl- N^2 -[4-(2-amino-1-trimethylsilyloxyethyl)-1-methylpyrazol-5-yl]formamide **56**, prepared by the reduction of N^1,N^1 -dimethyl- N^2 -[4-(cyano-trimethylsilyloxymethyl)-1-methylpyrazol-5-yl]formamide **57**, is a key stage in the synthesis of 1-methyl-1,4,5,6-tetrahydropyrazolo[3,4-*d*]-1,3-diazepin-4-ol **58**.^{39–41}

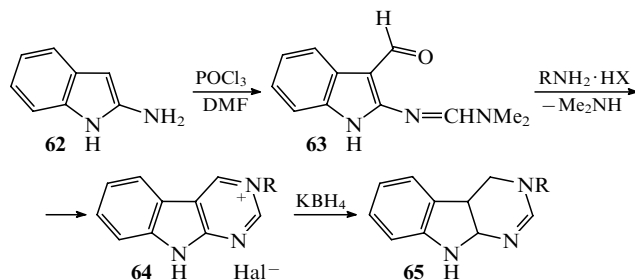


In the synthesis of 3*H*-2-thia-3,5,6-triazaacanthrylene **59**, the key intermediate, formamide **60**, containing a free amino group, is prepared using the Gewald heterocyclisation of N^1,N^1 -dimethyl- N^2 -(4-methyl-3-cyanoquinolin-2-yl)formamide **61**.⁴²



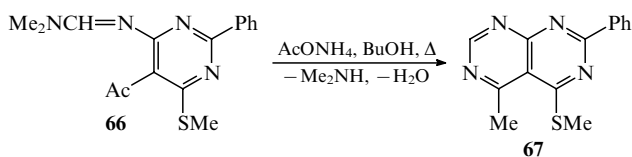
The reactions of compounds containing cyano-, ester or cabonyl group in the position adjacent to the amidine substituent with ammonia derivatives (see Table 1, reactions *d–j*) are widely used to form a fused pyrimidine fragment. In some cases, the reaction with ammonia is accompanied by deamidation.

On treatment with excess Vilsmeier reagent, reactive amino-substituted heterocyclic compounds are converted into formylhetarylformamides.⁴³ For example, 2-aminoindole **62** was used to synthesise N^1,N^1 -dimethyl- N^2 -(3-formylindol-2-yl)formamide **63**.⁴⁴ Refluxing this product with ammonium salts in ethanol induces cyclisation giving rise to salt **64** the subsequent reduction of which affords 3-substituted 2,3,4,4*a*-tetrahydropyrimido[4,5-*b*]indole **65**. This type of cyclisation has been studied in relation to hetarylformamides derived from 3-aminoindole^{45,46} or 3- and 5-aminopyrazoles.^{47,48}

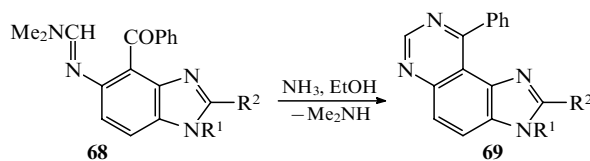


X = Cl, Br; R = CH₂COOH, Et, Ph, (CH₂)₂NMe₂, (CH₂)₃OH.

The behaviour of hetarylformamides having an acetyl group in the position adjacent to the amidine substituent with respect to low-basicity nitrogen-containing nucleophiles is similar to the behaviour of formyl-substituted derivatives.^{49,50} Thus N^1,N^1 -dimethyl- N^2 -(5-acetyl-6-methylthio-2-phenylpyrimidin-4-yl)formamide **66** is converted into 5-methyl-4-methylthio-2-phenylpyrimido[4,5-*d*]pyrimidine **67** when heated with ammonium acetate in butyl alcohol.⁵¹

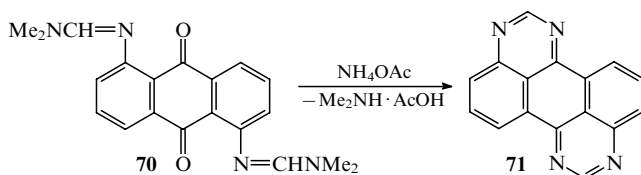


1,2-Disubstituted N^1,N^1 -dimethyl- N^2 -(4-benzoyl-1*H*-benzimidazol-5-yl)formamide **68**, containing a low-reactivity carbonyl group, is transformed into substituted 9-phenyl-3*H*-imidazo[4,5-*f*]quinazoline **69** only upon prolonged heating in an ethanol solution of ammonia in an autoclave.⁵²



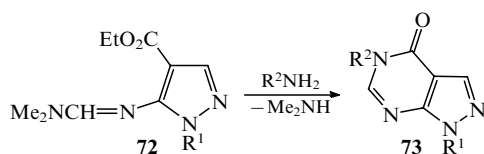
R¹ = CH₂CH₂OH, Ph; R² = H, Me.

The carbonyl groups of anthraquinone can also be involved in the amidine cyclisations.^{53,54} For example, 1,5-bis(3-methyl-1,3-diazabut-1-enyl)-9,10-dioxo-9,10-dihydroanthracene **70** is converted into 1,3,7,9-tetraazaperylene **71** on refluxing with ammonium acetate in ethylene glycol methyl ether.⁵⁵ This reaction proved convenient for the synthesis of anthrapyrimidine dyes.^{56,57}



The reactions of alkylamines with hetarylformamides containing an ethoxycarbonyl group next to the amidine substituent provide the possibility of constructing a pyrimidone fragment. Thus ethyl 5-(3-methyl-1,3-diazabut-1-enyl)-1*H*-pyrazolyl-4-carboxylates **72** were used to synthesise 5-substituted pyrazolo[3,4-*d*]pyrimidin-4-

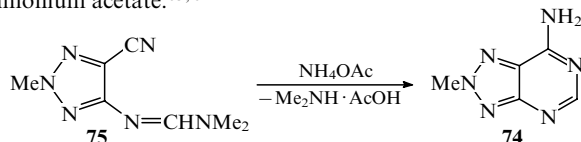
ones **73**.⁵⁸ 3-Benzyl-7-methylpyrido[2,3-*d*]pyrimidin-4-one was prepared in a similar way from the corresponding pyridine derivative.⁵⁹



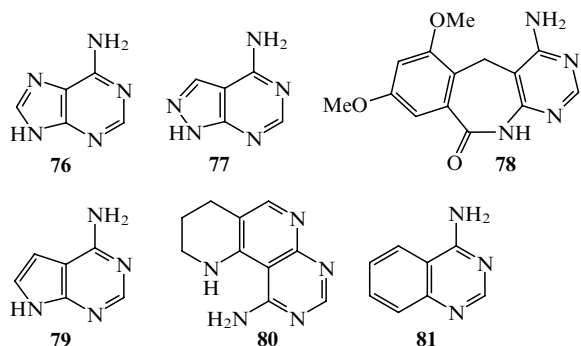
$R^1 = \text{H, Ph; } R^2 = \text{CH}_2\text{Ph, CH}_2\text{CH}_2\text{Ph, MeCHCH}_2\text{Ph.}$

The reactions of nitriles with nitrogen-containing nucleophiles are widely used to synthesise heterocyclic compounds.^{60,61} Thus the reactions of aryl- and hetaryl-formamidines containing a cyano group in the position adjacent to the amidine substituent with ammonia, amines or their salts were found to be convenient for the preparation of fused aminopyrimidines. This approach is used in combinatorial chemistry.⁶²

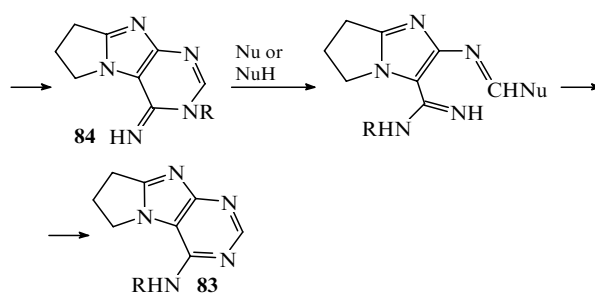
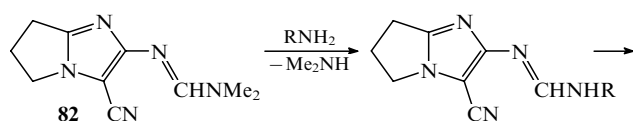
7-Amino-2-methyl-2*H*-1,2,3-triazolo[4,5-*d*]pyrimidine **74** was obtained by refluxing *N*¹,*N*¹-dimethyl-*N*²-(5-cyano-2-methyl-2*H*-1,2,3-triazol-4-yl)formamidine **75** in an aqueous solution of ammonium acetate.^{63,64}



The same strategy was employed to prepare adenine **76**,⁶⁵ 4-aminopyrazolo[3,4-*d*]pyrimidine **77**,^{66–69} 4-amino-6,8-dimethoxy-5-hydrobenzo[*e*]pyrimido[4,5-*b*]azepin-10-one **78**,⁷⁰ 4-aminopyrrolo[2,3-*d*]pyrimidine **79**,⁷¹ 5,6,7,8-tetrahydro-1,3,5,10-tetraazaphenanthren-4-ylamine **80**,⁷² 4-aminoquinazoline **81**⁷³ and their derivatives.

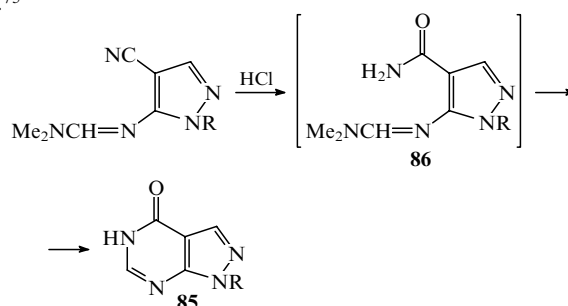


The transformation of *N*¹,*N*¹-dimethyl-*N*²-(3-cyano-5,6,7-trihydropyrrolo[1,2-*a*]imidazol-2-yl)formamidine **82** into substituted 4-amino-5,6,7-trihydropyrrolo[2,1-*f*]purines **83** has been studied and a mechanism has been proposed for this reaction.⁷⁴ Presumably, the reaction starts with transamination at the formamidine carbon atom, accompanied by evolution of dimethylamine. This is followed by an intramolecular attack by the NH group on the cyano carbon atom giving rise to 5-substituted 4-imino-5,6,7-trihydropyrrolo[2,1-*f*]purines **84**. On treatment with nucleophiles, the products **84** undergo the Dimroth rearrangement; as a result, the aminopyrimidine fragment adds to the initial heterocyclic system.

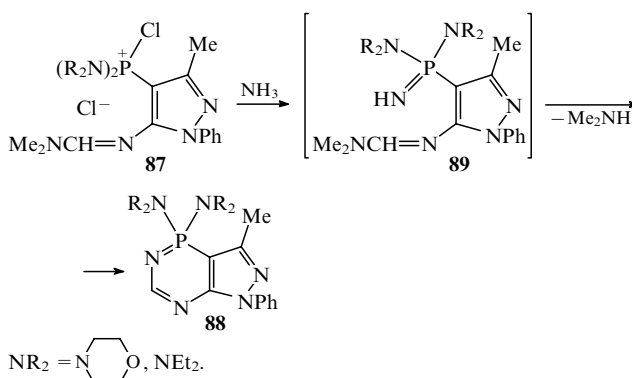


$\text{Nu} = \text{OH}^-, \text{EtO}^-; \text{NuH} = \text{HOH, EtOH, RNH}_2.$

Partial hydrolysis of hetarylformamidines containing a cyano group in the position adjacent to the amidine group is accompanied by heterocyclisation which gives a pyrimidone fragment. Thus treatment of 5-dimethylaminomethylideneamino-4-cyanopyrazoles substituted at the 1-position yields pyrazolo[3,4-*d*]pyrimidin-4-ones **85**. Apparently, the cyclisation proceeds *via* amides **86**.⁷⁵

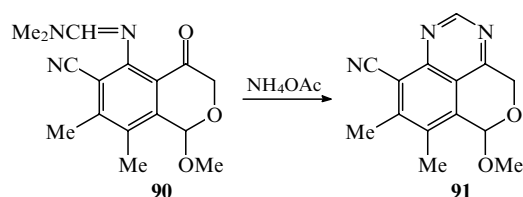


Cyclisation of hetarylformamidines can be used to prepare organophosphorus compounds.^{76,77} For example, the phosphorus salts **87** cyclise on treatment with ammonia to yield 3-methyl-4,4-bis(amino)-1-phenylpyrazolo[4,5-*e*]-1,3,4λ⁵-diazaphosphinines **88** *via* intermediate iminophosphonic diamides **89**.⁷⁸

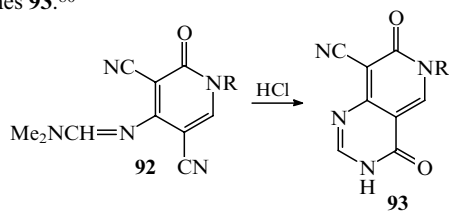


$\text{NR}_2 = \text{N(CH}_2\text{CH}_2\text{O)}_2, \text{NEt}_2.$

When the amidine molecule incorporates two different reaction sites which occupy positions neighbouring the amidine group, the more reactive site participates predominantly in the cyclisation. For instance, *N*¹,*N*¹-dimethyl-*N*²-(1-methoxy-7,8-dimethyl-4-oxo-6-cyanoisochroman-5-yl)formamidine **90** is converted into 6-methoxy-7,8-dimethyl-4*H*,6*H*-5-oxa-1,3-diazaphenylene-9-carbonitrile **91**, the cyano group remaining intact during the reaction.⁷⁹

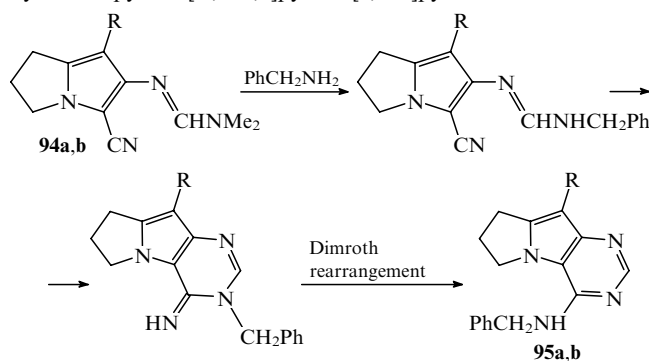


The same functional groups located in different positions of the heterocycle can differ substantially in reactivity. Thus heterocyclisation of dicyano-substituted 4-dimethylaminomethylideneamino-2-oxo-1,2-dihydropyridines **92** occurs selectively giving rise to 8-cyano-4,7-dioxo-3,4,6,7-tetrahydropyrido[4,3-*d*]pyrimidines **93**.⁸⁰



R = Ph, 4-MeC₆H₄, 4-BrC₆H₄.

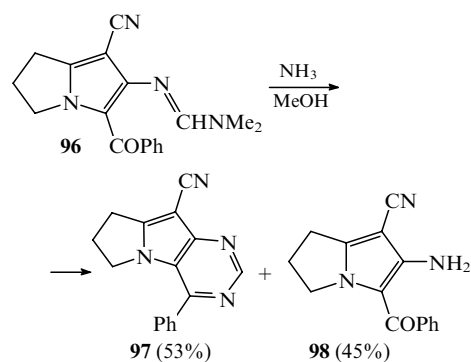
The reaction of *N*¹,*N*¹-dimethyl-*N*²-(5,7-dicyano-2,3-dihydro-1*H*-pyrrolizin-6-yl)formamidine **94a** with benzylamine involves the 5-cyano group and results in 8-benzylamino-4-cyano-2,3-dihydro-1*H*-pyrrolo[1',2':5,1]pyrrolo[2,3-*d*]pyrimidine **95a**. The second cyano group does not participate in the reaction. In the case where different functional groups are present in the positions neighbouring the amidine substituent, the cyclisation pathway depends not only on the reactivity of each group but also on their positions in the ring. Indeed, in the cyclisation of *N*¹,*N*¹-dimethyl-*N*²-(5-cyano-7-ethoxycarbonyl-2,3-dihydro-1*H*-pyrrolizin-6-yl)-formamidine **94b**, the more reactive cyano group is involved in the reaction, which affords 8-benzylamino-4-ethoxycarbonyl-2,3-dihydro-1*H*-pyrrolo[1',2':5,1]pyrrolo[2,3-*d*]pyrimidine **95b**.⁸¹



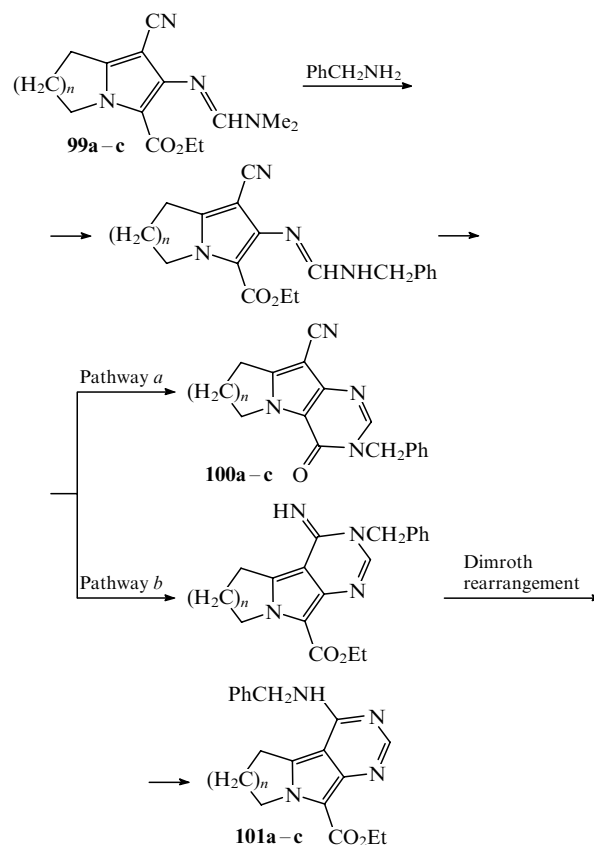
R = CN (a), COOEt (b).

The fact that the reaction follows only this pathway can appear unexpected because the α -position of the unsubstituted pyrrole ring is enriched in electron density, and the cyclisation would rather be expected to involve the electrophilic substituent located in the less electron enriched β -position. However, the presence of two electron-withdrawing groups induces redistribution of the partial charges on the carbon atoms of the ring in both the ground and transition states. As a consequence, the electronic effects of the heterocyclic fragment of the molecule substantially change. In the above example, the reactivity of the nitrile group in the α -position of the pyrrole ring increases and, hence, cyclisation is highly regioselective. The assumption concerning electron density redistribution is supported by the fact that the ester groups at the 4-position of 2,4-pyrroledicarboxylic acid diesters are more stable against hydrolysis than the 2-ester groups.⁸²

In the case of 5-benzoyl-7-cyano-6-(3-methyl-1,3-diazabut-1-enyl)-2,3-dihydro-1*H*-pyrrolizine **96**, the carbonyl group is much more reactive than the nitrile group; therefore, cyclisation affords 4-cyano-8-phenyl-2,3-dihydro-1*H*-pyrrolo[1',2':5,1]pyrrolo[2,3-*d*]pyrimidine **97**. The reaction is accompanied by deamidation, which gives compound **98**.⁸³



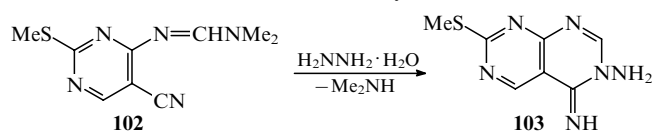
Kadushkin *et al.*⁸⁴ have studied the influence of the size of the ring fused to the pyrrole fragment on the pathway of cyclisation of polymethylenepyrrole derivatives, namely, 7-cyano-6-dimethylaminomethylideneamino-5-ethoxycarbonyl-2,3-dihydro-1*H*-pyrrolizine **99a**, 1-cyano-2-dimethylaminomethylideneamino-3-ethoxycarbonyl-5,6,7,8-tetrahydroindolizine **99b** and 1-cyano-2-dimethylaminomethylideneamino-3-ethoxycarbonyl-6,7,8,9-tetrahydro-5*H*-pyrrolo[1,2-*a*]azepine **99c**.



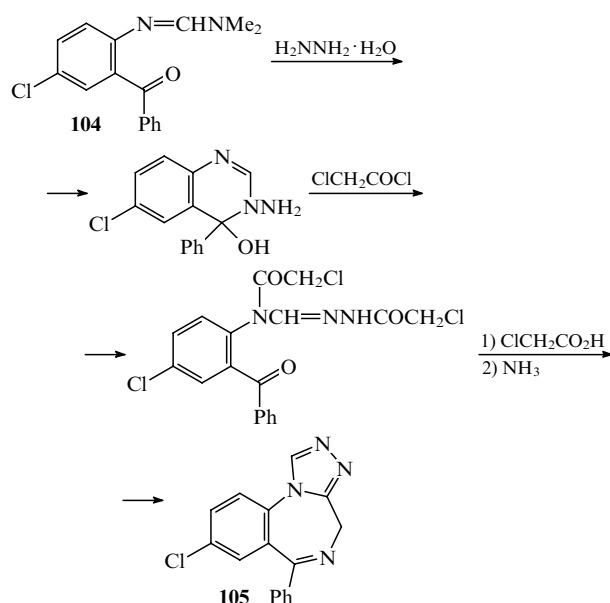
Compound	<i>n</i>	Yield (%)	
		100	101
a	1	< 5	79
b	2	40	42
c	3	95	< 5

In the case of the compound **99a**, pathway *b* predominates, *i.e.* the reaction involves the nitrile group and gives compound **101a**. When the ring size and, hence, steric overcrowding, increases, the heterocyclisation involves the ethoxycarbonyl group activated by the neighbouring heterocyclic fragment. The contribution of pathway *a* increases and, correspondingly, the compounds **100b,c** are formed in higher yields.

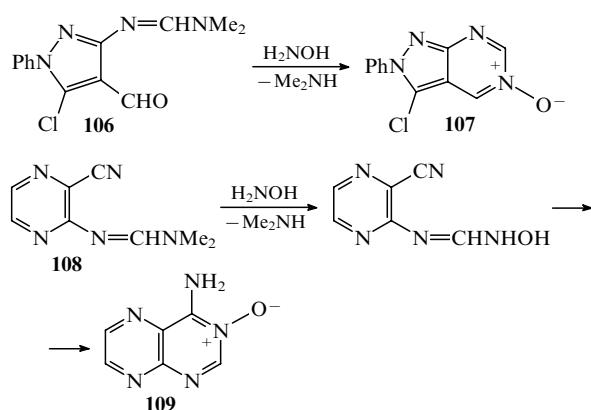
Hydrazine hydrate is also used to perform cyclisation of hetarylformamidines containing a nitrile or carbonyl group in the position adjacent to the amidine substituent. Thus 5-cyano-4-dimethylaminomethylideneamino-2-methylthiopyrimidine **102** reacts with hydrazine hydrate being thus converted into 3-amino-4-imino-7-methylthio-3,4-dihydropyrimido[4,5-*d*]pyrimidine **103**.⁸⁵ However, in some cases, only deamidination is observed in these reactions instead of cyclisation.⁸⁶



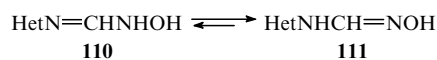
Since the formation of a pyrimidine ring is more favourable than the formation of a 1,2,4-triazepine ring,⁸⁷ only one nitrogen of the hydrazine molecule participates in the cyclisation.^{88–90} The free amino group can be used in subsequent transformations. Thus the reaction of *N*¹,*N*¹-dimethyl-*N*²-(2-benzoyl-4-chlorophenyl)formamidine **104** with hydrazine hydrate has served as the first stage in the synthesis of *symm*-triazolo[4,3-*a*]-1,4-benzodiazepine derivatives **105**.⁹¹



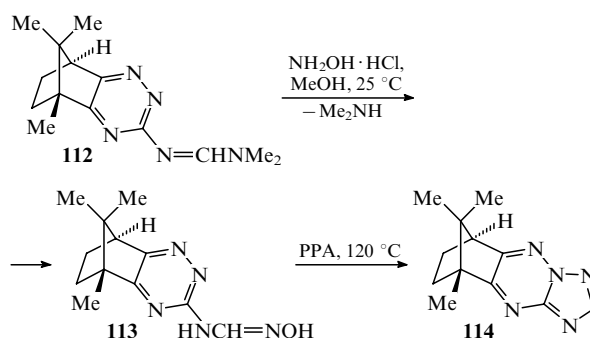
Treatment with hydroxylamine of hetarylformamidines containing a carbonyl or cyano group neighbouring an amidine group gives rise to pyrimidine *N*-oxides.^{44–47, 92, 93} For instance, 5-chloro-3-dimethylaminomethylideneamino-4-formyl-1-phenylpyrazole **106** was converted into 3-chloro-5-oxy-2-phenylpyrazolo[3,4-*d*]pyrimidine **107**, while 3-cyano-2-dimethylaminomethylideneaminopyrazine **108** was transformed into 4-amino-3-oxypyridine **109**.



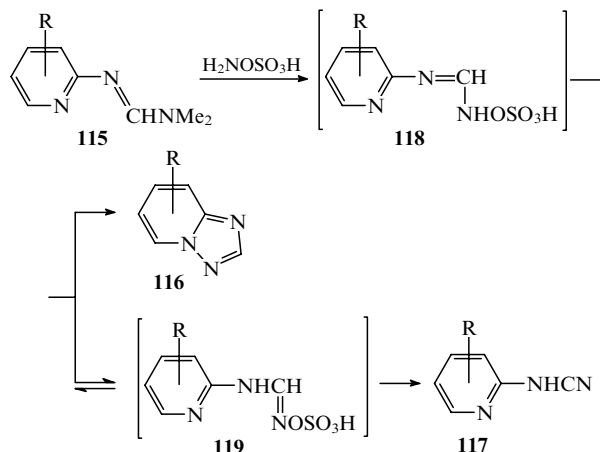
It should be emphasised that, unlike the reactions with ammonia, hydrazine or their salts, in this case, the initial product of replacement of the dialkylamino group **110** can be detected and, in some instances, isolated. This difference is due to the fact that the initial reaction product **110** is equilibrated with its tautomer **111**, the latter predominating in the reaction mixture. Compounds of the type **111** do not tend to undergo heterocyclisation, which proceeds more slowly.



N-Hetarylformamidines in which the amidine substituent occupies the neighbouring position with respect to the pyridine-type nitrogen atom⁹⁴ can be used to synthesise fused heterocycles containing a 1,2,4-triazole fragment.⁹⁵ For example, 4-dimethylaminomethylideneamino-1,11,11-trimethyl-3,5,6-triazatricyclo-[6.2.1.0^{2,7}]undeca-2,4,6-triene **112** was converted into 11,14,14-trimethyl-3,4,5,7,9-pentacyclo[9.2.1.0^{2,9}.0^{4,8}]tetradeca-2,5,7,9-tetraene **113** in a high yield.⁹⁶ The triazole fragment (compound **114**) is formed upon nucleophilic attack by a ring nitrogen atom on the nitrogen atom attached to the hydroxy group in the product **113** formed in the reaction with hydroxylamine. The cyclisation occurs on treatment with polyphosphoric acid (PPA) with heating. The high potential of this approach was also demonstrated in relation to derivatives of pyridine,⁹⁷ pyrimidine,⁹⁸ pyridazine,⁸⁹ pyrazine,⁹⁹ *symm*-triazine and some other polycyclic systems.^{73, 100, 101}



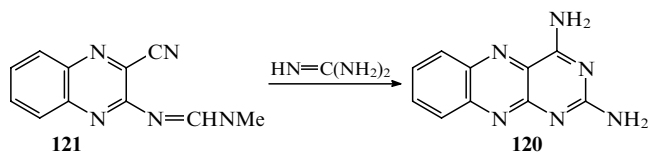
Apparently, cyclisation induced by hydroxylaminesulfuric acid follows a similar route.^{102, 103} Thus *N*¹,*N*¹-dimethyl-*N*²-2-pyridylformamidine derivatives **115** are converted into the corresponding 1,2,4-triazolo[1,5-*a*]pyridines **116**. 2-Pyridylcyanoamides **117** are formed as side products. Presumably, the dimethylamino group is initially replaced by hydroxylaminesulfuric acid giving rise to compound **118**, which cyclises. The side product **117** is produced from tautomer **119**.



R = H, 2-Me, 3-Me, 4-Me.

When hetarylformamidines containing a cyano group near the amidine function are subjected to cyclisation on treatment with

guanidine, two amino groups are incorporated simultaneously into the pyrimidine ring formed. This approach was used to prepare 2,4-diaminopyrimido[4,5-*b*]quinoxaline **120** from 3-cyano-2-dimethylaminomethylideneaminoquinoxaline **121**.¹⁰⁴

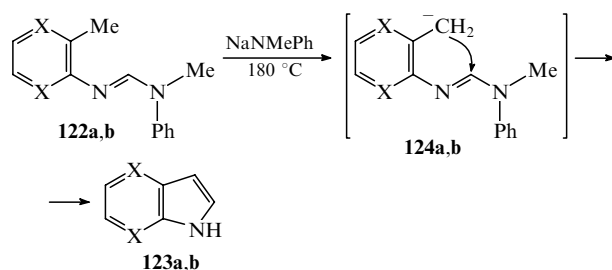


2. Reactions involving C-nucleophiles

Cyclisations of hetarylamidines in which the substitution of the amidine amino group gives rise to a C–C bond are presented in a general form in Table 2.

As in the case of *N*-nucleophiles, this approach permits the construction of five-, six- and seven-membered heterocycles.

Aryl- and hetarylformamidines containing a methyl group next to an amidine group are converted into heteroannulated pyrroles on heating with sodium phenylmethylamide in methyl-aniline.^{105, 106} Thus 2-dimethylaminomethylideneamino-3-



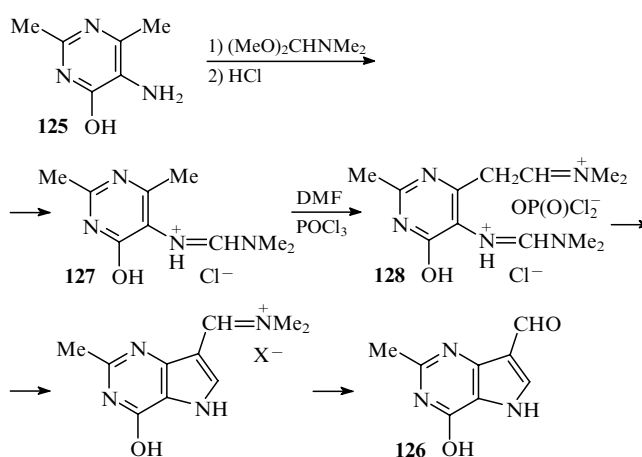
X = N (a), CH (b).

Table 2. Products of cyclisation of hetarylamidines formed on treatment with C-nucleophiles.

Type of reaction	Hetarylamidine	Reagent or reaction conditions	Reaction product
a		B: or flash pyrolysis	
b		POCl ₃ –DMF	
c		Δ	
d		B:	
e		CF ₃ CO ₂ H	
f		B:	
g		B:	

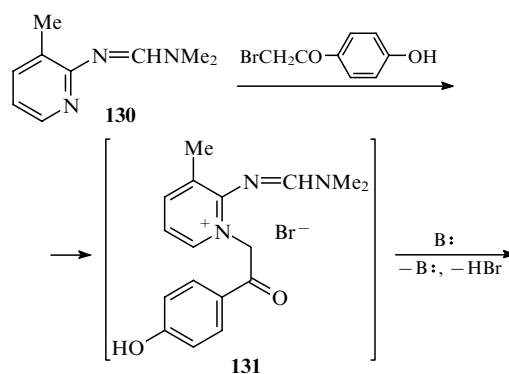
methylpyrazine **122a** is transformed into 5*H*-pyrrolo[2,3-*b*]pyrazine **123a**. The indole **123b** was prepared from *N*¹,*N*¹-dimethyl-*N*²-2-tolylformamidine **122b** in a similar way. This process can be regarded as a modified Madelung synthesis of indoles.¹⁰⁷ The reaction occurs in the presence of strong bases *via* intermediate carbanions **124a,b**, or under conditions of vacuum flash pyrolysis.¹⁰⁸

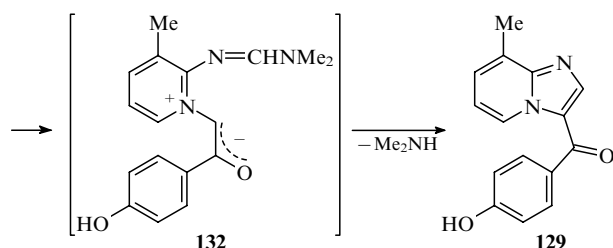
Treatment of heterocyclic compounds having methyl and amino groups in the vicinal positions with excess Vilsmeier reagent results in the formation of a pyrrole fragment containing a β-formyl group.^{109, 110} For example, 5-amino-4-hydroxy-2,6-dimethylpyrimidine **125** was converted into 4-hydroxy-2-methyl-5*H*-pyrrolo[3,2-*d*]pyrimidine-7-carbaldehyde **126**.¹¹¹ The first stage gives amidinium salt **127**, which is then formylated at the methyl group by the Vilsmeier reagent. The CH-acidity of the methylene group in intermediate **128** is enhanced, which facilitates heterocyclisation. The amidinium salt **127** does not cyclise when heated in DMF in the absence of POCl₃, which confirms the proposed mechanism.¹¹¹



X = Cl, OP(O)Cl₂.

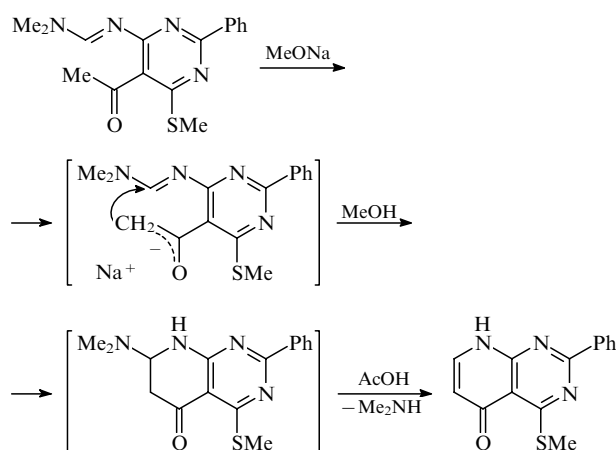
When hetarylamidines in which the pyridine nitrogen atom occupies an adjacent position to the amidine substituent are made to react with halo ketones, fused imidazole-containing heterocycles are produced. For example, 3-(4-hydroxybenzoyl)-8-methylimidazo[1,2-*a*]pyridine **129** was prepared by the reaction of *N*¹,*N*¹-dimethyl-*N*²-(3-methylpyridin-2-yl)formamidine **130** with 2-bromomethyl 4-hydroxyphenyl ketone. In this process, the pyridine nitrogen atom is alkylated to give intermediate **131**. The high CH-acidity of the methylene group in this compound¹¹² ensures easy cyclisation, which proceeds *via* enolate anion **132**. Therefore, the basicity of the amidine substituent is normally sufficient for the subsequent transformations.



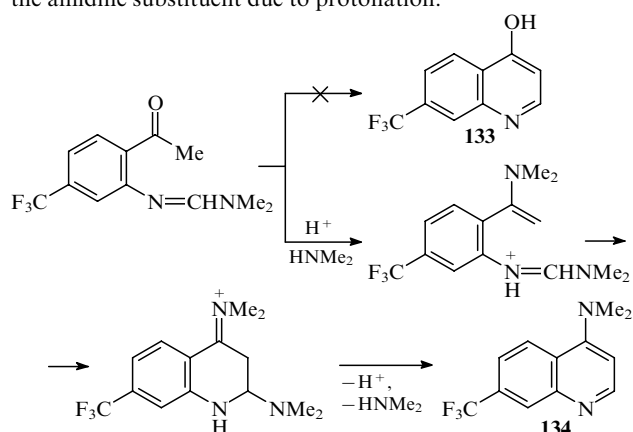


Despite the ambident properties of the enolate anion **132**, the process follows only the route involving the attack of the C-nucleophile on the electron-deficient formamidine centre; after elimination of dimethylamine, this results in the formation of a fused imidazole ring. This reaction has been used to synthesise derivatives of imidazo[1,2-*a*]pyridine,¹¹³ imidazo[1,2-*a*]pyrimidine,¹¹⁴ imidazo[1,2-*b*]-1,2,4-triazine,¹¹⁵ imidazo[2,1-*b*]thiazole,¹¹⁶ imidazo[2,1-*b*]-1,3,4-thiadiazole, pyrrolo[1,2-*a*]imidazole¹¹⁷ and so on.

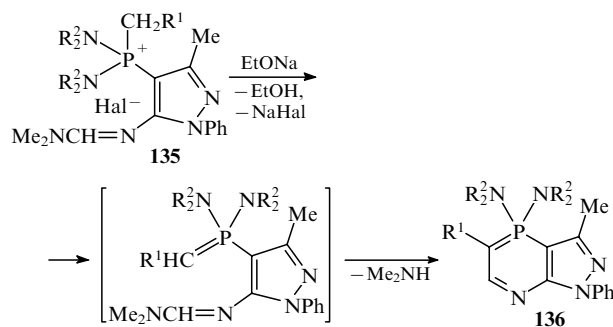
The enolate anion generated from hetarylamidines having an acetyl substituent in the position adjacent to the amidine fragment also acts as a C-nucleophile. Intramolecular heterocyclisation results in the annelation of a pyridone fragment.¹¹⁸ For example, 4-methylthio-2-phenyl-5-oxo-8*H*-pyrido[2,3-*d*]pyrimidine was prepared from 5-acetyl-4-dimethylaminomethylideneamino-2-phenyl-6-thiomethylpyrimidine.



Cyclisation of 2-(3-methyl-1,3-diazabut-1-enyl)-4-trifluoromethylacetophenone yields 4-dimethylamino-7-trifluoromethylquinoline **134** instead of the expected 4-hydroxy-7-trifluoromethylquinoline **133**.¹¹⁹ This unusual behaviour was explained by assuming that oxygen is replaced by dimethylamine at the stage of enolisation. The decrease in the nucleophilicity on passing from the enolate anion to enamine is counterbalanced, in the opinion of the authors, by the increase in the electrophilicity of the amidine substituent due to protonation.

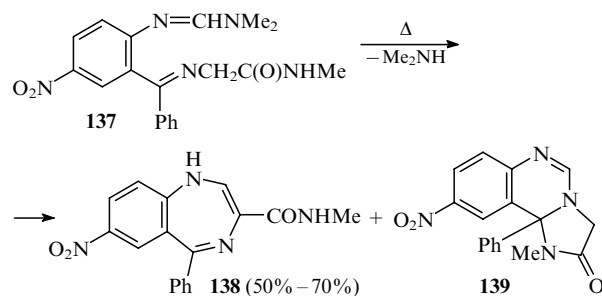


Phosphonium ylides generated from pyrazolylphosphonium salts **135** undergo intramolecular heterocyclisation *in situ* giving rise to pyrazolo[5,4-*b*]-1,4λ⁵-azaphosphinines **136**.^{76, 78, 120} 4-Nitrobenzylphosphonium salts cyclise much more easily than methylphosphonium salts because of their higher CH-acidity.



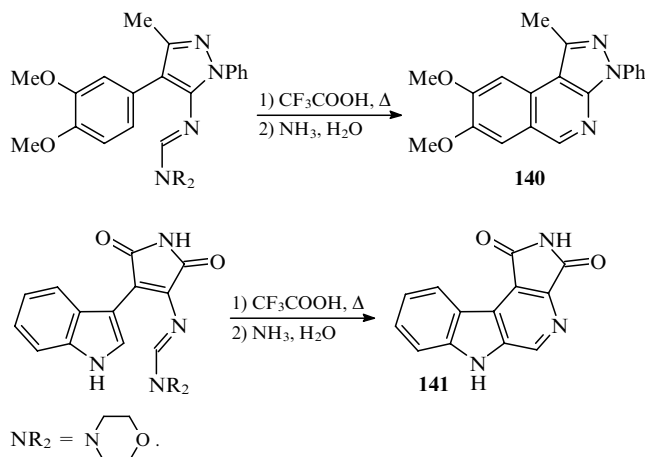
$R^1 = \text{H}$, $\text{Hal} = \text{I}$; $R^1 = 4\text{-NO}_2\text{C}_6\text{H}_4$, $\text{Hal} = \text{Br}$; $\text{NR}_2^2 = \text{N} \begin{smallmatrix} \diagup \diagdown \end{smallmatrix} \text{O}$, NEt_2 .

Heating of *N*-methyl-(2-dimethylaminomethylideneamino-5-nitrophenyl)-phenylmethylideneaminoacetamide **137** gives 3-methylaminocarbonyl-7-nitro-5-phenyl-1*H*-benzo[*e*]-1,4-diazepine **138** as the major product.¹²¹ In the opinion of the authors, cyclisation occurs through the substitution of the enolate anion for the dimethylamino group.



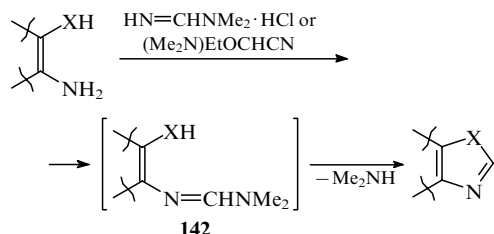
The side product, 1-methyl-9-nitro-10*b*-phenyl-1,10*b*-dihydroimidazo[1,2-*c*]quinazolin-2-one **139**, results apparently from an intramolecular cyclisation of the aza-Cope type of the product of rearrangement of the initial compound **137**.

The electrophilicity of the amidine substituent markedly increases upon protonation. This was used to synthesise 7,8-dimethoxy-1-methyl-3-phenylpyrazolo-[3,4-*c*]isoquinoline **140** and 6*H*-pyrrolo[3,4-*c*]carboline-1,3-dione **141** from the corresponding formamidines.^{122, 123} Cyclisation occurs upon refluxing in trifluoroacetic acid over a period of 8–12 h.



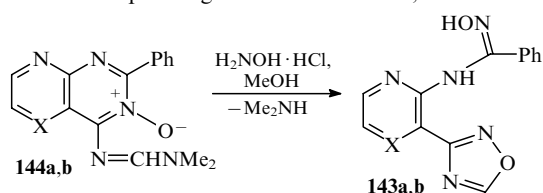
3. Reactions involving O- and S-nucleophiles

N,N-Dimethylformamidine hydrochloride and dimethylaminoethoxyacetonitrile are mild reagents used to transform the amino group into the amidine group. However, when they were made to react with 1,2-hydroxyamino or 1,2-sulfanylamino compounds, no amidines were produced; only cyclisation products — annelated oxazoles or thiazoles — were isolated instead. The formation of functionalised amidine intermediates **142** in these reactions was just postulated.² Aminophenols, aminobenzenethiols or the corresponding pyrimidine and pyridazine derivatives were used as the initial compounds.



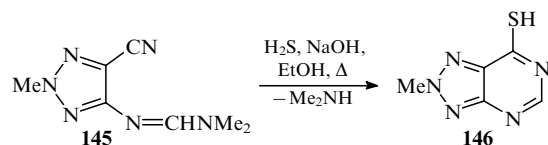
X = O, S.

The systems containing an *N*-oxide fragment in the adjacent position to the amidine substituent are more stable; however, they undergo recyclisation on heating or on treatment with hydroxylamine salts.^{124, 125} For example, *N*-hydroxy-*N'*-(1,2,4-oxadiazol-3-yl)pyridin-2-yl)benzamidines **143a** and *N*-hydroxy-*N'*-(1,2,4-oxadiazol-3-yl)pyridazin-2-yl)benzamidines **143b** were prepared from the corresponding formamidines **144a,b**.

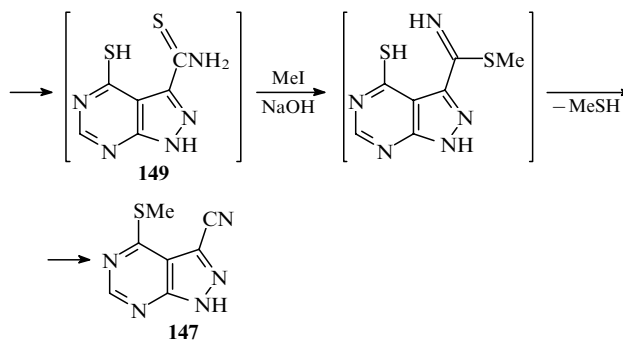
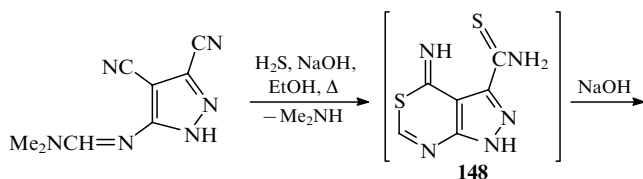


X = CH (a), N (b).

Treatment of hetarylformamidines containing a nitrile group next to the amidine group with hydrogen sulfide in the presence of bases is used to furnish a pyrimidinethiol fragment.¹²⁶ This method was used, for example, to transform 5-cyano-4-dimethylaminomethylideneamino-2-methyl-2*H*-1,2,3-triazole **145** into 2-methyl-7-thioxo-2*H*-1,2,3-triazolo[4,5-*d*]pyrimidine **146**.



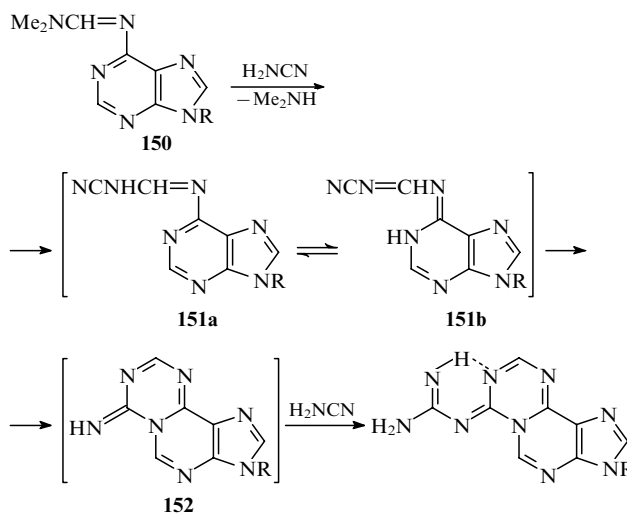
A similar reaction was used⁶⁶ in the synthesis of 3-cyano-4-methylthiopyrazolo[3,4-*d*]pyrimidine **147** from 3,4-dicyano-5-dimethylaminomethylideneamino-1*H*-pyrazole. It was suggested that 4-imino-3-thiocarbamoyl-1,4-dihydropyrazolo[3,4-*d*]-1,3-thiazine **148** undergoes the Dimroth rearrangement to give intermediate **149**. The compound **149** reacts with MeI to give the reaction product **147**.



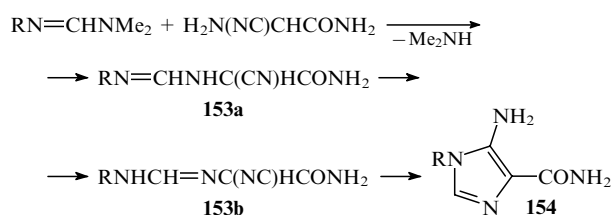
IV. Other heterocyclisation reactions

This Section surveys transformations of different types in which nucleophilic substitution at the formamidine carbon atom or cycloaddition involving the C = N fragment are not the key stages in the synthesis of heterocyclic compounds. The leading role in these reactions is played by polyfunctional reagents which react with the amidine or by transformations of the heterocyclic fragment of *N*-hetarylformamidines.

In the general case, during cyclisation of trisubstituted aryl- and hetarylformamidines with functionalised nitriles, first, the amidine amino group is replaced and subsequently *N*-nucleophilic heterocyclisation occurs. Thus the reaction of 6-dimethylaminomethylideneamino-9*H*-purine **150** with cyanamide starts with substitution of cyanamide for the dimethylamino group to give derivative **151a**; heterocyclisation resulting in 3-substituted 7-imino-3*H*-1,3,5-triazino[2,1-*i*]purine **152** occurs in the tautomer **151b**. The compound **152** reacts *in situ* with excess cyanamide to be converted into 7-amidinoimino-3*H*-1,3,5-triazino[2,1-*i*]purine.¹²⁷

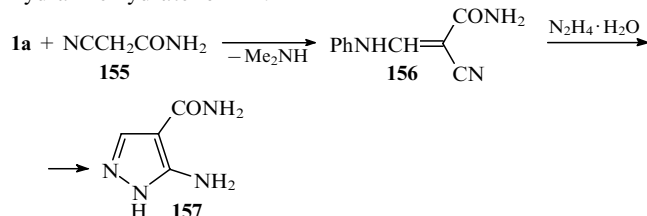


Trisubstituted formamidines react with aminocyanacetamide according to the transamination pattern. The resulting *N,N'*-disubstituted amidines **153a** are equilibrated with their tautomers **153b**; the latter undergo cyclisation to give imidazole derivatives **154** due to the reaction between the NH and CN groups.¹²⁸ This strategy has also been employed in the synthesis of purine derivatives.^{129, 130}



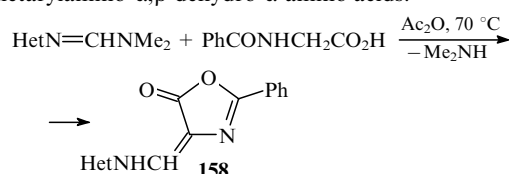
R = Ph (**1a**), Bn.

Highly basic N^1, N^1 -dimethyl- N^2 -phenylformamidine **1a** performs two functions in the reaction with cyanoacetamide **155**; first, it facilitates the transformation of cyanoacetamide into the carbanion on heating, and, second, it acts as the substrate in which this carbanion substitutes the dimethylamino group. The reaction yields 3-anilino-2-cyanoacrylamide **156**, which is converted into pyrazole derivative **157** on refluxing in an aqueous solution of hydrazine hydrate for 1 h.¹³¹

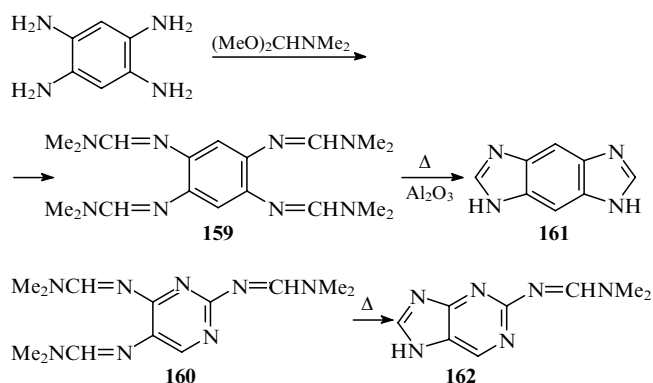


In this reaction, the amidine, like triethyl orthoformate, acts as a one-carbon synthon for the synthesis of pyrazole derivatives.

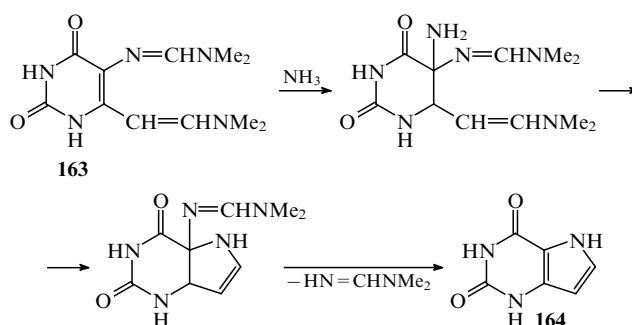
When N -hetarylformamidines are heated with hippuric acid in acetic anhydride, nucleophilic substitution at the formamidine carbon atom is accompanied by heterocyclisation. This reaction has been performed for pyridine, pyrimidine, pyrazine, pyridazine, oxazole and benzo-2,1,3-thiadiazole derivatives.¹³² Compounds of the type **158** are the key intermediates in the synthesis of β -hetaryl-amino- α, β -dehydro- α -amino acids.^{133–136}



Aromatic or heteroaromatic compounds containing more than two electron-donating substituents in the ring, including 1,2-diamino derivatives, behave unusually when made to react with dimethylformamide dimethyl acetal. These reactions can give bis- or even tetrakis-amidines, instead of fused imidazoles, for example, 1,2,4,5-tetrakis(dimethylaminomethylideneamino)benzene **159** and 2,4,5-tris(dimethylaminomethylideneamino)benzene **160**. Apparently, the [2-aminoaryl(hetaryl)]amidines formed initially cannot undergo cyclisation because of the low electrophilicity of the formamidine carbon atom. The corresponding fused imidazole-containing heterocyclic compounds — benzo-[1,2- d :4,5- d']diimidazole **161** and 2-dimethylaminomethylideneaminopurine **162** — can be prepared by subsequent pyrolysis in the presence of Al_2O_3 or on heating in diethylene glycol.^{137, 138}

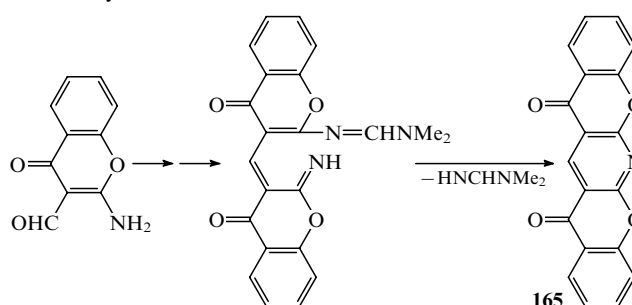


The amidine substituent can also function as a leaving group in heterocyclisation. Thus 5-dimethylaminomethylideneamino-6-(2-dimethylaminovinyl)pyrimidine-2,4-dione **163** is converted into pyrrolo[3,2- d]pyrimidine-5,7-dione **164** on treatment with ammonia.¹³⁹

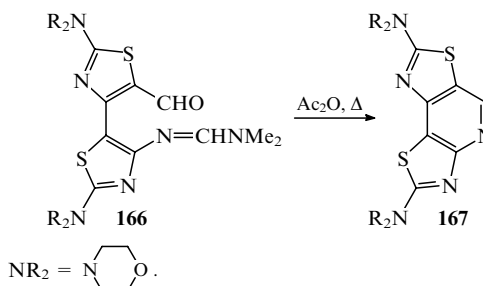


According to this scheme, ammonia adds to the double bond of the heterocycle, being attached to the more electrophilic carbon atom at the α -position relative to the carbonyl group.

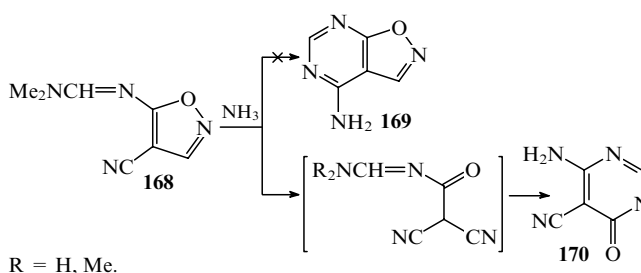
A similar transformation has been used to prepare 5,7-dioxo-6-aza-12,14-dione **165** from 2-amino-4-oxo-4 H -chromenyl-3-carbaldehyde.¹⁴⁰



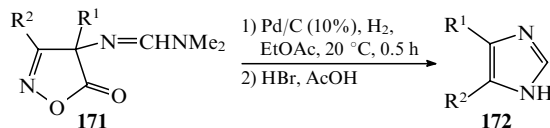
Partial deamidation occurs during the cyclisation of 4'-dimethylaminomethylideneamino-2,2'-dimorpholino-5-formyl-[4,5'-b]thiazole **166**, giving rise to 2,7-dimorpholinothiazolo[4,5- b]thiazolo[4,5- d]pyrimidine **167**.¹⁴¹



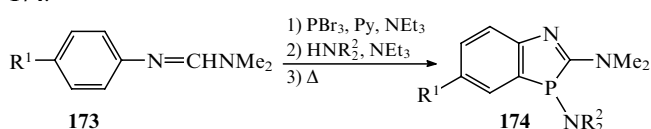
The ease of cleavage of the isoxazole ring at the N—O bond on treatment with nucleophiles or upon reduction accounts for the non-classical behaviour of isoxazolylamidines under heterocyclisation conditions. For example, when 4-cyano-5-dimethylaminomethylideneaminoisoxazole **168** is treated with a hot aqueous solution of ammonia, instead of the expected formation of 4-aminoisoxazolo[5,4- d]pyrimidine **169** or hydrolysis of the amidine substituent, recyclisation occurs giving rise to 4-amino-5-cyanopyrimidin-6-one **170**.¹⁴²



The reduction of 4-dimethylaminomethylideneaminoisoxazol-5-ones **171** catalysed by palladium supported on carbon affords imidazoles **172** in high yields¹⁴³ (90–95%). The key stage of the heterocyclisation is apparently intramolecular transamination at the formamidine carbon atom by the iminocarbonyl function, resulting from reduction of the N–O bond.



Formamidines react with trivalent phosphorus halides in the presence of bases to give molecules with a phosphorus–formamidine carbon bond.^{144, 145} This approach has been used to synthesise phosphorus-containing heterocyclic compounds. For example, treatment of *N*¹,*N*¹-dimethyl-*N*²-arylformamidines **173** with PBr_3 in the presence of bases followed by treatment with secondary amines and heating affords 3*H*-benzaazaphospholes **174**.^{146, 147}



$\text{R}^1 = \text{Me}_2\text{N}, \text{MeO}, \text{Me}, \text{H}, \text{Br}; \text{R}^2 = \text{Me}, \text{Et}, \text{Pr}^i.$

V. Conclusion

The data considered here, which are concerned with heterocyclisation of *N*¹,*N*¹-disubstituted *N*²-aryl- and *N*²-hetarylformamidines, clearly demonstrate the high synthetic potential of these compounds and the prospects for using them to synthesise various heterocyclic systems, including those difficult to prepare otherwise.

However, it should be noted that the synthetic capacities of these compounds are far from being exhausted. The diverse reactivity of amidines is determined by the electrophilicity of the amidine carbon atom, the strong electron-donating ability of the amidine substituent, and the possibility of being involved in nucleophilic reactions and in pericyclic reactions of various types. In general, this allows not only annelation of five-, six- or seven-membered heterocycles to the rings present initially but also one-stage preparation of their functional derivatives by varying the functional substituents in the initial amidines, the reaction conditions and the reagents used for cyclisation.

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^a — *Chem. Heterocycl. Compd. (Engl. Transl.)*

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^d — *Russ. J. Org. Chem. (Engl. Transl.)*

Monoorganyl derivatives of tellurium(IV)

A A Maksimenko, A V Zakharov, I D Sadekov

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Abstract. Data on the synthesis, reactions and structures of monoorganyl derivatives of tellurium(IV) (σ -telluranes) RTeX_3 are systematised and generalised. The use of these compounds in preparative organic chemistry is considered. The bibliography includes 238 references.

I. Introduction

Derivatives of tetracoordinate tellurium RTeX_3 (X is an anionoid substituent) belong to the so-called σ -telluranes. Compounds R_2TeX_2 and tetraorganyltelluranes R_4Te are also σ -telluranes. σ -Telluranes RTeX_3 are important starting compounds in the synthesis of various organic derivatives of tellurium. Thus cyclisation of aryl- and arylvinyltellurium trichlorides is a method for the preparation of various tellurium-containing heterocycles, which is specific to the chemistry of organotellurium compounds. In addition, detelluration and halodetelluration of σ -telluranes RTeX_3 are used in organic synthesis. The two last-mentioned fields of application of monoorganyl derivatives of tellurium(IV) are based on the electrophilic properties of the trichlorotellurium group and a low (compared to other chalcogens) energy of the C–Te bond. σ -Telluranes are also characterised by higher stabilities compared to analogous sulfur and selenium derivatives because the higher energy levels of the p orbitals of tellurium are favourable for bonding.^{1,2} Thus sulfur compounds RSCl_3 decompose to give RSCl and Cl_2 even at very low temperature, RSeCl_3 are stable at room temperature but decompose to RSeCl and Cl_2 on heating, whereas RTeCl_3 are stable up to their melting points.³

Previously, σ -telluranes RTeX_3 have been considered in a review (see Ref. 4) and in the corresponding sections of monographs (see Refs 3 and 5–7).

II. Methods of synthesis

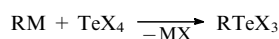
Most compounds of the RTeX_3 type have been prepared from tellurium tetrachloride and diorganyl ditellurides as the starting compounds. Various derivatives of RTeX_3 can also be synthesised by anion exchange in organyltellurium trihalides. Approaches

based on the use of hexahalotellurates, complexes of tellurium tetrachloride with aromatic amines, tellurinic acids and their anhydrides have been studied to a substantially lesser extent. The corresponding reactions were either examined for a few compounds or afforded a limited number of compounds.

1. Reactions of tellurium tetrahalides with heteroorganic compounds

The most important preparative procedures for the synthesis of organyltellurium trihalides involve exchange reactions of tellurium tetrahalides with heteroorganic compounds. These reactions were used primarily for the preparation of aryltellurium trichlorides and aryltellurium tribromides. Poor solubility of TeI_4 in non-polar solvents and its decomposition in polar solvents prevent its use in the synthesis of tellurium triiodides.

In principle, a general procedure for the synthesis of organyltellurium trihalides could involve reactions of equimolar amounts of tellurium tetrahalides with organolithium or -magnesium compounds.



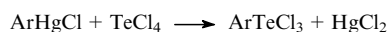
M = Li, MgX; X = Cl, Br.

However, these reactions afford complex mixtures of products due to a more profound exchange. Nevertheless, the reaction of 2-biphenyllithium with TeCl_4 gave rise to 2-biphenyltellurium trichloride, albeit in low yield (16%).⁸

(*N,N*-Dimethylcarbamoyl)tellurium trichloride **1** was prepared by the reaction of TeCl_4 with dimethylaminocarbonylsodium and isolated as a complex with DMF.⁹



Organyltellurium trihalides can be synthesised by the reactions of tellurium tetrahalides with organic derivatives of Hg, Si, Sn or Pb. The procedure most generally employed involves the reaction of TeCl_4 with organomercury compounds. This procedure has been used for the synthesis of aryltellurium trichlorides **2**. Unlike telluration (see below) which yields *p*-substituted aryltellurium trichlorides, this procedure is more versatile because it allows one to synthesise compounds with any substituents (including electron-withdrawing groups) at any position.^{8, 10–21}

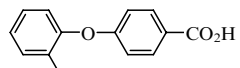
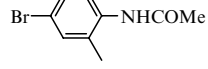
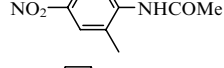
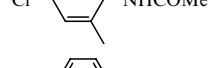
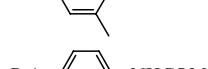
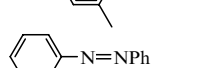
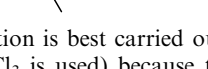
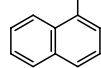
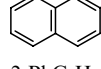
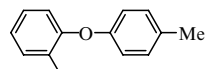


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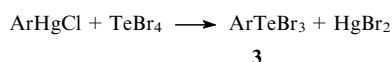
Received 17 April 2000

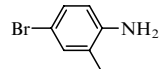
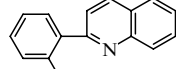
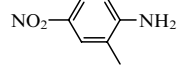
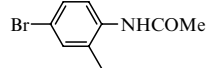
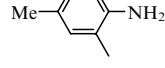
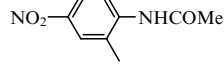
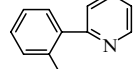
Uspekhi Khimii 69 (10) 940–962 (2000); translated by T N Safonova

Ar	Ref.	Ar	Ref.
	17		10
C ₆ F ₅	14, 15		13
4-BrC ₆ H ₄	16		21
4-ClC ₆ H ₄	16		21
4-NO ₂ C ₆ H ₄	16		19
3-FC ₆ H ₄	16		19
3-NO ₂ C ₆ H ₄	16		19
4-MeC ₆ H ₄	11, 16		18
Ph	11, 16		
	13		
	12		
2-PhC ₆ H ₄	8		
4-PhNHC ₆ H ₄	20		
	10		

The above-mentioned reaction is best carried out in anhydrous dioxane (sometimes CHCl₃ is used) because the resulting mercury(II) chloride forms a 1 : 1 complex with dioxane, which is poorly soluble at room temperature. Generally, the aryltellurium trichlorides formed in admixture with HgCl₂ and, hence, it is necessary to purify the reaction products by recrystallisation or to reduce them to diaryl ditellurides followed by chlorinolysis.

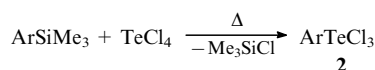
Arylmercury chlorides were used as the starting compounds in the synthesis of aryltellurium tribromides **3**. If molecules of the initial organic substrates contain amino groups²² or the substrates represent pyridine^{23, 24} or quinoline derivatives,²⁴ their reactions with TeCl₄ afford mixtures of unidentified compounds due apparently to side complexation reactions. In this case, TeBr₄ is more suitable.



Ar	Ref.	Ar	Ref.
	22		24
	22		21
	22		21
	23, 24		

Organyltellurium trihalides can also be synthesised from silicon or tin derivatives or, less often, lead or germanium derivatives. The reactivities of heteroorganic derivatives R₄E (E = Si, Ge, Sn or Pb) and R₃EX (X = Cl or Br) increase as the atomic weight of the element increases. The derivatives of the R₄E type are more reactive than R₃EX. Compounds R₂EX₂ and R₃EX do not react with tellurium tetrahalides. The Ar–E bond in mixed derivatives ArEAlk₃ is cleaved under the action of electrophilic tellurium tetrahalides. Thus aryltellurium trichlorides **2** were prepared in 65%–80% yields upon refluxing a mixture of

equimolar amounts of aryltrimethylsilanes and TeCl₄ in toluene for 1 h.^{25, 26}

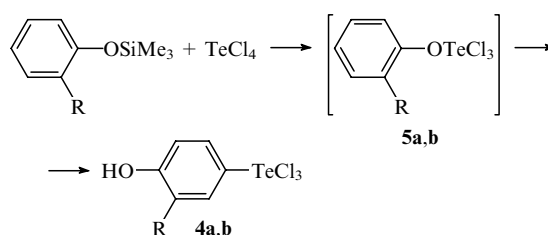


Ar = 4-BrC₆H₄, Ph, 4-MeC₆H₄, 3-MeC₆H₄, 2-C₆H₄CH₂Ph.

In benzyltrimethylsilane, the C_{sp³}–Si bond is inert with respect to TeCl₄. Refluxing of equimolar amounts of these compounds in toluene afforded a mixture of 4-Me₃SiCH₂C₆H₄–TeCl₃ and (4-Me₃SiCH₂C₆H₄)₂TeCl₂.²⁷

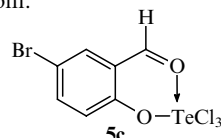
The corresponding aryltrimethylsilanes were used for the synthesis of bis(trichlorotelluro)benzenes. Thus 1,4-bis(trichlorotelluro)benzene²⁸ and 1,2-bis(trichlorotelluro)benzene²⁹ were prepared in ~ 50% yields upon refluxing equimolar amounts of TeCl₄ and 1,4-bis(trimethylsilyl)benzene or 1,2-bis(trimethylsilyl)benzene, respectively, in 1,2-dichlorobenzene.

4-Hydroxyaryltellurium trichlorides **4** were synthesised by the reactions of aryl trimethylsilyl ethers with TeCl₄ in boiling toluene in yields higher than 80%.³⁰

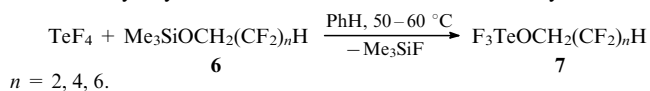


R = H (**a**), Me (**b**).

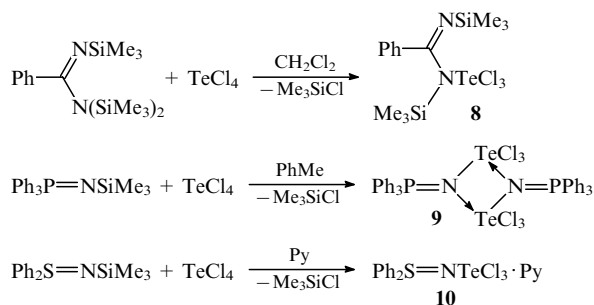
It was assumed³⁰ that the reaction proceeded *via* intermediate aryloxytellurium trichlorides **5** followed by rearrangement into compounds **4**. This mechanism was supported by the synthesis of aryloxytellurium trichloride **5c** from TeCl₄ and the trimethylsilyl ether of 5-bromosalicylaldehyde.³⁰ Apparently, this compound is stabilised due to coordination of tellurium to the carbonyl oxygen atom.



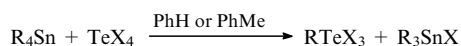
The reactions of TeF₄ with silylated perfluoroalkanols **6** afforded aryloxytellurium trifluorides **7** in 76%–82% yields.³¹



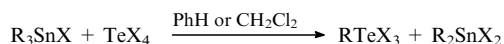
N-Trichlorotellurioamines **8**,³² **9**³³ and **10**³⁴ were synthesised by the reactions of the corresponding *N*-trimethylsilyl derivatives with TeCl₄.



Organotin compounds react with tellurium tetrahalides at room temperature.^{35–38} The yields of organytellurium trihalides vary from moderate to very high.



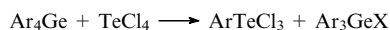
X	R	Ref.	X	R	Ref.
Cl	Me	35	Br	Me	35
	Et	35		Et	35
	Pr	35		Pr	35
	Ph	35, 36		Ph	35
	4-MeC ₆ H ₄	37			



X	R	Ref.	X	R	Ref.
Cl	Et	38	Br	Et	38
	Ph	36		Ph	38

The reaction of tributylphenylstannane with TeCl₄ resulted in the cleavage of the C(Ar)–Sn bond to form phenyltellurium trichloride in 80% yield.³⁷

Tetraarylgermanes react with tellurium tetrachloride like organotin derivatives.³⁷

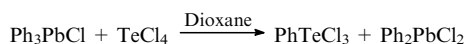


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Ar = Ph, 4-MeC₆H₄.

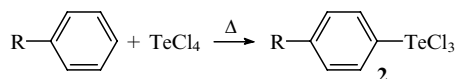
Germanium derivatives Ar₃GeCl do not react with TeCl₄.³⁷

Tetraarylplumbanes react with TeCl₄ to form diaryltellurium dichlorides even under mild conditions.³⁹ Phenyltellurium trichloride was prepared with the use of Ph₃PbCl.³⁹



2. Reactions of TeCl₄ with activated arenes

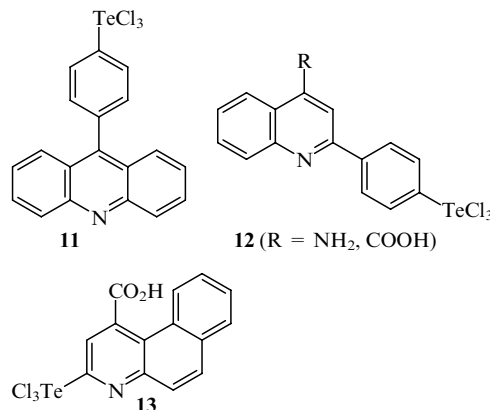
The salt-like structure of tellurium tetrachloride, *viz.*, [TeCl₃]⁺Cl[−] (see Refs 40–44) or [TeCl₃]⁺[TeCl₅][−] (see Ref. 45), both in the solid state and in solutions was confirmed by IR and Raman spectroscopy^{40–45} and the data on conductivity.^{41,42} This compound exhibits moderate electrophilicity and can be involved in electrophilic substitution (telluration) with arenes containing electron-donor substituents. The telluration is highly regioselective. The trichlorotellurio group enters exclusively into the *para* position with respect to the electron-donor substituent in the ring.^{13,16,27,46–56} Heating of azobenzene with TeCl₄ afforded 2-trichlorotellurioazobenzene.⁵⁷ The yields of aryltellurium trichlorides **2** vary over a wide range.



R	Ref.	R	Ref.
OH	46	OPr	16
Br	47	OBu	16
Me	48, 49	OPh	56
CH ₂ SiMe ₃	27	OAc	16
OMe	16, 46, 50–52	SMe	16
OCH ₂ CO ₂ Me	53	SPh	13
OEt	16, 46, 51, 54, 55	NHAc	46

Morgan and Drew⁵⁵ were the first to demonstrate the high selectivity of telluration. He prepared bis(4-ethoxyphenyl) ditelluride by reduction of the product of the reaction of TeCl₄ with phenetole and demonstrated that the reaction of the ditelluride with nitric acid afforded exclusively 4-nitrophenetole. This selectivity was also proved by IR and ¹H NMR spectroscopy for a large number of compounds.

However, C-telluration does not occur if the benzene ring of compounds contains such a strong electron-donor substituent as the dimethylamino group; instead, the complex 2Me₂NPh · TeCl₄ is formed.^{58,59} Analogous complexes were also obtained from other aromatic amines.^{59–62} The corresponding tellurium trichlorides can be isolated from these complexes by subsequent treatment (see below). A decrease in the basicity of nitrogen prevents complexation with TeCl₄. For example, acetanilide underwent telluration in the *para* position.⁴⁶ Organyltellurium trichlorides **11–13** were synthesised from the corresponding derivatives of acridine or quinoline and TeCl₄ in CCl₄.⁶³



However, other quinolines and acridines,⁶³ various pyridines,^{42,45,60,63–65} indoles, carbazoles,⁶³ Schiff's bases^{66–69} and hydrazones⁷⁰ react with tellurium tetrachloride to form only molecular complexes.

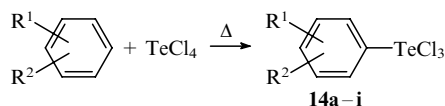
Aromatic compounds containing electron-withdrawing substituents (nitrobenzene or 4-nitroanisole) do not react with TeCl₄,⁵⁰ whereas refluxing of TeCl₄ with benzonitrile led to trimerisation of the latter yielding 2,4,6-triphenyltriazine.⁴⁷

Under ordinary conditions, benzene does not react with TeCl₄ due to which it can be used in telluration as the solvent along with CHCl₃ and CCl₄. The introduction of one methyl group into the benzene ring leads to only weak activation of the ring with respect to telluration. Although prolonged boiling (20 h) of a solution of TeCl₄ in toluene afforded 4-methylphenyltellurium trichloride in 83% yield,⁴⁹ toluene can be used as the solvent in certain reactions of TeCl₄ with sufficiently reactive arenes.¹⁶

The TeCl₃ group possesses strong electron-withdrawing properties (see Section IV). Only one trichlorotellurium group can be introduced into the ring by telluration, unlike mercuration, which often gives rise to polymercurated compounds.

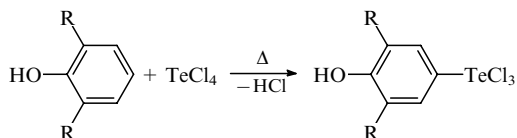
Polynuclear hydrocarbons, for example, naphthalene, react with TeCl₄ without additional activation of their nuclei by introducing electron-donor substituents. The reaction of TeCl₄ with naphthalene in toluene under conditions of kinetic control afforded 1-trichlorotellurionaphthalene in 24% yield,¹⁶ which agrees with the usual direction of electrophilic substitution in naphthalene. However, prolonged heating of naphthalene with TeCl₄ at 110 °C without a solvent (under conditions of thermodynamic control) gave rise to 2-trichlorotellurionaphthalene in 54% yield.⁷¹ The reaction of anthracene with TeCl₄ afforded a mixture of 9-chloro- and 9,10-dichloroanthracenes.⁷²

In the case of arenes containing two substituents, the TeCl₃ group is introduced in the *para* position with respect to the stronger electron-donor substituent.^{16,48,50,55,73–75} If this position is occupied, the introduction occurs in the *ortho* position to this substituent.⁵⁰



Compound 14	R ¹	R ²	Ref.
a	4-Me	3-Me	48
b	4-OMe	3-Me	50
c	4-OMe	2-MeO	55
d	4-OMe	3-MeO	16
e	4-OMe	3-OH	55
f	4-OH	3-Me	73
g	4-OH	2-Cl	74
h	4-OH	3-Cl	74
i	2-OMe	5-Me	75

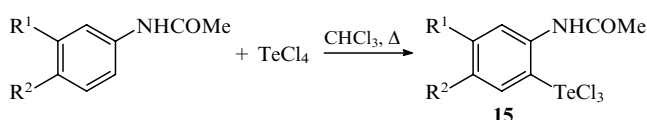
Telluration of dialkylphenols occurs in the *para* position with respect to the hydroxy group.⁷⁵



R = Me, Bu^t.

The reactions of TeCl₄ with 4-bromoanisole and 3-methoxytoluene also gave rise to aryltellurium trichlorides.⁵⁰ However, the position of the introduction of the trichlorotellurium group into the ring was not established.⁵⁰

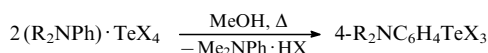
Acetamidophenyltellurium trichlorides **15** were synthesised by telluration of 3-mono- and 3,4-disubstituted acetanilides.¹⁹



R¹ = R² = Me; R¹ = Me, OH, OMe, SMe; R² = H.

Aryltellurium tribromides and triiodides cannot be prepared by telluration of arenes with tellurium tetrabromide or tetraiodide, respectively, even in the case of such active compounds as anisole, phenetole or veratrole. Apparently, this is associated with a decrease in electrophilicity of tellurium tetrahalides TeX₄ on going from chlorine to iodine. The electrophilicity of tellurium tetrachloride can be increased by forming complexes of TeCl₄ with Lewis acids. In particular, the complex [TeCl₃]⁺[AlCl₄][−] was formed with AlCl₃.^{43,76} Bergman⁴⁷ was the first to use this approach. However, prolonged boiling of the components in the presence of catalytic amounts of AlCl₃ afforded a mixture of aryltellurium trichlorides and diaryltellurium dichlorides. A more convenient procedure was proposed by Gunther *et al.*⁷⁷ The reactions are carried out with a two-to-threefold excess of AlCl₃. The course of the reaction is monitored by measuring the amount of hydrogen chloride evolved, and the reaction is stopped after evolution of one equivalent of HCl.

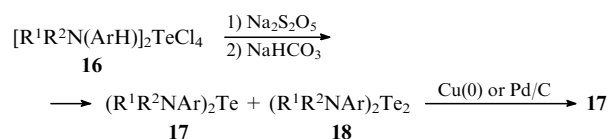
As mentioned above, direct telluration of arenes containing NR₂ substituents (R = H or Alk) cannot be performed because these compounds form 2 : 1 complexes with tellurium tetrahalides, which are poorly soluble in ordinary solvents (benzene, toluene or chloroform). Prolonged boiling of these complexes in anhydrous MeOH under an inert atmosphere did lead to electrophilic substitution at the *para* position with respect to the NR₂ group.⁶¹



R = H, Me; X = Cl, Br.

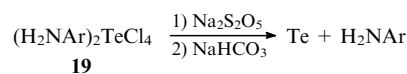
However, attempts to synthesise 4-dimethylaminophenyltellurium trichloride by this procedure failed.⁵⁹ It is believed⁵⁹ that 2 : 1 complexes of aromatic amines with TeCl₄ can have different structures depending on the nature of the amines. In the complexes with *N*- and *ortho*-substituted amines **16**, the tellurium-containing group is located at position 4 with respect to the NR¹R² group. Reduction of these complexes affords mixtures of

4-amino-substituted diaryl tellurides **17** and the corresponding diaryl ditellurides **18**. The ditellurides **18** can be converted into the tellurides **17** by treatment of the reaction mixture with a copper powder or Pd/C. The yields of the diaryl tellurides **17** vary over a wide range (8% – 72%).⁵⁹



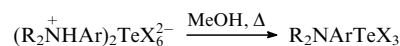
R¹R²NAr = 4-Me₂NC₆H₄, 4-MeNHC₆H₄, 4-PhNHC₆H₄, 4-H₂NC₆H₄, 4-H₂N-3-MeC₆H₃, 4-H₂N-3,5-Me₂C₆H₂, 4-H₂N-3-EtOC₆H₃, 4-H₂N-3-CF₃C₆H₃, 4-H₂N-3-MeOCOC₆H₃.

Reduction of 2 : 1 complexes of substituted anilines with TeCl₄ (**19**) gives rise to elemental tellurium and the corresponding anilines.⁵⁹



ArNH₂ = 4-MeC₆H₄NH₂, 3,5-Me₂C₆H₃NH₂, 3-O₂NC₆H₄NH₂, 2,4,6-Br₃C₆H₂NH₂.

The synthesis of *p*- or *o*-substituted aminophenyltellurium trihalides was carried out also with the use of hexahalotellurates of amines, which have been prepared in high yields from amines and solutions of tellurium tetrahalides in hydrohalic acids.^{61,62} Refluxing of these salts in anhydrous methanol was accompanied by elimination of HX to form the corresponding aminoaryltellurium trihalide. It was believed⁶² that hexahalotellurates in methanolic solutions exist in equilibrium with free amines and tellurium tetrahalides and the electrophilic substitution occurs at the nucleus of the free amine.

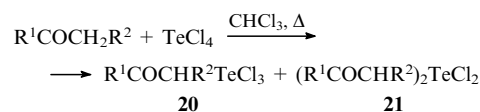


R₂NAr = 4-H₂NC₆H₄, 4-MeNHC₆H₄, 4-Me₂NC₆H₄, 4-H₂N-3-MeC₆H₃, 2-H₂N-5-MeC₆H₃, 2-H₂N-3,5-Me₂C₆H₂, 4-H₂N-3,5-Me₂C₆H₂; X = Cl, Br, I.

3. Reactions of TeCl₄ with compounds containing active methylene groups

The reactions of aliphatic compounds containing activated methyl or methylene groups with TeCl₄ can proceed as electrophilic substitution at the saturated carbon atom.

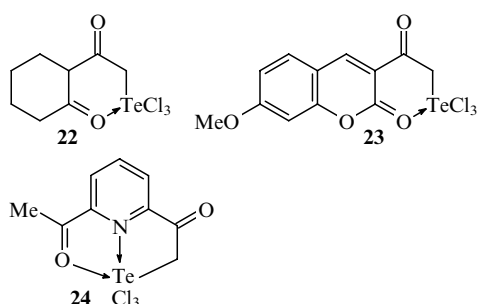
Generally, ketones containing at least one methylene group at the α position with respect to the carbonyl group react with TeCl₄ (a solution in CHCl₃) in a molar ratio of 2 : 1 to form mixtures of organytellurium trichlorides **20** and diorganytellurium dichlorides **21**. The trichlorides can be isolated provided that they are poorly soluble and form precipitates.^{78–82} In some cases, the trichlorides were obtained as the only reaction products in high yields.^{81,82} It was suggested⁷⁸ that the reaction proceeded through the addition of TeCl₄ at the double bond of the enol followed by elimination of HCl. Diisopropyl ketone did not react with TeCl₄.^{78,79}



R ¹	R ²	Ref.	R ¹	R ²	Ref.
Me	Me	78–80	Ph	Ph	78
Et	Me	78	4-ClC ₆ H ₄	H	82
Pr	H	80	2-HOC ₆ H ₄	H	82

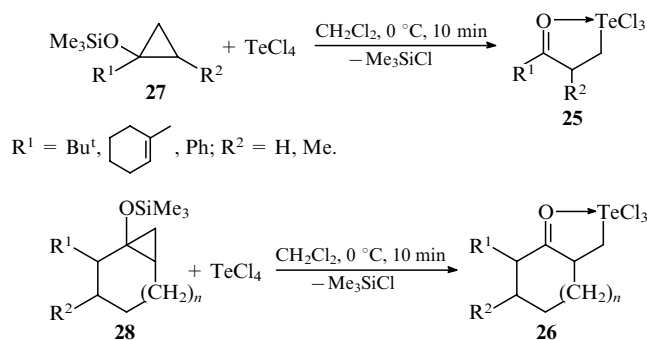
R ¹	R ²	Ref.	R ¹	R ²	Ref.
Pr	Et	78–80	3-MeOC ₆ H ₄	H	82
Bu ^t	H	78, 80	(CH ₂) ₆		81
Ph	Et	78	(CH ₂) ₇		81

The reactions of TeCl₄ with some polyfunctional ketones gave rise to organytellurium trichlorides of the type **20** as the only products.⁸³ Thus telluration of 2-acetylcyclohexanone, 3-acetyl-7-methoxycoumarin and 2,6-diacetylpyridine afforded trichlorides **22–24**, respectively. Apparently, the trichlorotellurium group in the compounds **22–24** exhibits low electrophilicity due to the formation of intramolecular O → Te coordinate bonds, and the reaction stops at this stage. The presence of intramolecular coordinate bonds was confirmed by IR and NMR spectroscopy and X-ray diffraction study of the trichloride **24** (see Section IV). The ketones **22–24** are more stable to hydrolysis than other organytellurium trichlorides, which was also attributed to intramolecular O → Te coordinate bonds.⁸³



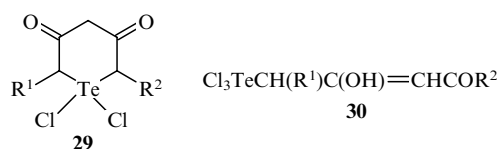
The compounds **22–24** have been used for the preparation of thermo- and photothermographic materials.⁸⁴

Trichlorotellurium ketones **25** and **26** containing the trichlorotellurium group at the β position with respect to the carbonyl group were prepared by the reactions of trimethylsilyloxycyclopropanes **27** and **28**, respectively, with TeCl₄ (the yields were 71%–93%).⁸⁵ The compounds **25** and **26** were subjected to dehydrotelluration without isolation from the reaction mixture (see Section III). Based on the IR spectral data, Nakahira *et al.*⁸⁵ assumed the presence of intramolecular O → Te coordinate bonds in the ketones **25** and **26**.



R¹ = R² = H, *n* = 2, 5; R¹–R² = (CH=CH)₂, *n* = 1.

In β-diketones, the most acidic hydrogen atoms of the methylene group are replaced by the TeCl₃ group only if the carbonyl groups bear aryl substituents. Thus the reaction of dibenzoylmethane with TeCl₄ afforded very unstable (dibenzoylmethyl)tellurium trichloride (PhCO)₂CHTeCl₃.⁸⁶ The reactions of TeCl₄ with β-diketones containing at least one hydrogen atom at each of the α- and α'-carbon atoms give rise to 1,1-dichloro-1-telluracyclohexane-3,5-diones **29** as the major products. Diorganytellurium dichlorides and organytellurium trichlorides **30** can be isolated in rare cases and only in reactions carried out in ethanol-free CHCl₃ as the solvent.^{87–89}



R¹, R² = Alk.

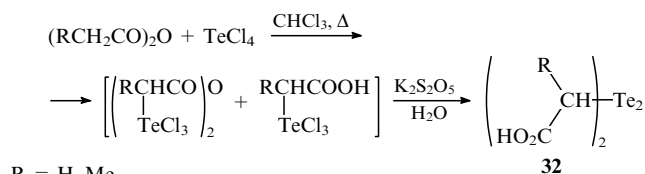
R ¹	R ²	Ref.
H	C ₆ H ₁₃	87
H	C ₈ H ₁₇	88
Pr	Pr	89

The formation of organytellurium trichlorides is favoured by the presence of two or three alkyl substituents at one of the α-carbon atoms and the presence of at least one hydrogen atom at the α'-carbon atom. If the organytellurium trichlorides formed bear at least one hydrogen atom at position 3 and chloroform used as the solvent has not been freed from EtOH, the reactions yielded tellurium trichlorides of ethyl enolates **31**.^{86–90} The position of the ethoxy group in these compounds has not been established unambiguously. However, taking into account the strong electron-withdrawing properties of the trichlorotellurium group, it can be assumed that the ethoxy group is located at the β position with respect to the TeCl₃ group.²²

R¹COCH=C(OEt)CR²R³TeCl₃

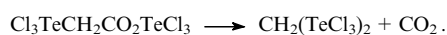
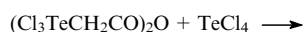
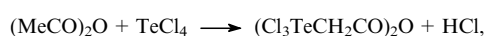
R ¹	R ²	R ³	Ref.
Me	H	H	90
Pr ⁿ	H	H	87
Pr ⁿ	H	Et	89
Pr ⁱ	H	H	87
Pr ⁱ	Me	Me	88
Bu ^t	H	H	86
Pr ⁱ CH ₂	H	H	87
Ph	H	H	86
Et	H	Me	87

The reactions of tellurium tetrachloride with acetic or propionic anhydrides taken in a ratio of 1:2 in CHCl₃ afforded mixtures of the corresponding α-trichlorotellurocarboxylic acids and anhydrides.^{50,91} However, these trichlorides were converted without isolation into ditellurides **32** under the action of an aqueous solution of K₂S₂O₅.



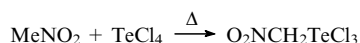
R = H, Me.

Methylenebis(tellurium trichloride) was isolated in low yield from the mixture obtained by the reaction of TeCl₄ with acetic anhydride.⁹¹ Later, this compound was prepared by refluxing a mixture of TeCl₄ with Ac₂O (taken in a molar ratio of 3:1) in CHCl₃ in 52% yield.⁹² The mechanism of formation of methylenebis(tellurium trichloride) was proposed.⁹²



Attempts to perform telluration of anhydrides of higher aliphatic acids resulted only in elimination of tellurium to form resinous products.

Of other compounds containing the active methylene group, nitromethane was subjected to telluration.⁹³

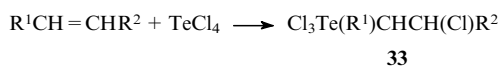


4. Addition of tellurium tetrachloride to multiple bonds

The major and, apparently, the only procedure for the preparation of alkanes and alkenes containing the TeCl_3 groups and the chlorine atoms at the vicinal positions involves the electrophilic addition of TeCl_4 to double or triple bonds.

a. Reactions of TeCl_4 with alkenes

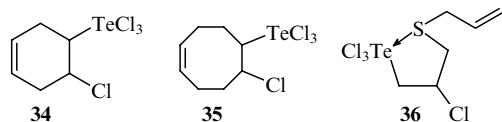
Under mild conditions (0–60 °C), TeCl_4 adds to the double bond of acyclic or cyclic alkenes to form β -chloroalkyl- and β -chlorocycloalkyltellurium trichlorides **33**.^{94–104} The reactions are generally performed in CHCl_3 , CCl_4 or MeCN . In some cases, bis(β -chloroalkyl)- and bis(β -chlorocycloalkyl)tellurium dichlorides are formed along with the corresponding trichlorides. The addition of TeCl_4 proceeds regioselectively. Thus the reactions of TeCl_4 with terminal alkenes occur as a Markovnikoff addition.



R^1	R^2	Ref.	R^1	R^2	Ref.
H	H	97	Me	Me	99, 100
H	Me	96, 98	$(\text{CH}_2)_3$		99, 100
H	Et	96	$(\text{CH}_2)_4$		94–96, 100, 102–104
H	Bn	101	$\text{CH}_2\text{CH}(\text{Me})(\text{CH}_2)_2$		103, 104
H	C_8H_{17}	99, 100	$(\text{CH}_2)_6$		99, 100
D	C_8H_{17}	99, 100			

The direction of the reactions of TeCl_4 with alkenes and primarily with cycloalkenes depends substantially on the temperature. Thus the reactions of cyclohexene and 4-methylcyclohexene with TeCl_4 in CHCl_3 , CCl_4 or MeCN at 25 °C gave rise to the adducts **33**, whereas the reactions carried out with boiling afforded benzene and toluene, respectively, as the major products.^{103, 104}

Dienes containing isolated double bonds, *viz.*, 1,4-cyclohexadiene¹⁰⁴ and 1,5-cyclooctadiene,^{104, 105} also react with tellurium tetrachloride. In these cases, TeCl_4 adds to only one double bond to form organytellurium trichlorides **34** and **35** in 49% and 64% yields, respectively. Diallyl sulfide reacts analogously to give the trichloride **36**, which is stabilised by an intramolecular S–Te coordinate bond (2.763 Å).¹⁰⁶

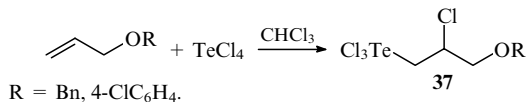


Unlike dienes containing isolated double bonds, cyclic dienes with conjugated double bonds (1,3-cyclohexadiene and 1,3-cyclooctadiene) react with TeCl_4 to form primarily dichlorocycloalkenes.¹⁰⁴

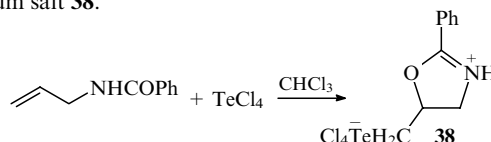
The stereochemistry of the addition of TeCl_4 to alkenes has been studied.¹⁰⁰ Thus the reactions of (*Z*)- and (*E*)-but-2-enes generally give rise to mixtures of isomers due to competitive *syn*- and *anti*-addition. *p*-Benzoquinone as a substrate favours the formation of a *syn*-addition product. It is believed that the stereospecific *syn*-addition occurs more or less according to a concerted mechanism. The free-radical reaction competes with this addition.

The addition of aryltellurium trichlorides to alkenes, unlike that of TeCl_4 , occurs nonstereoselectively.

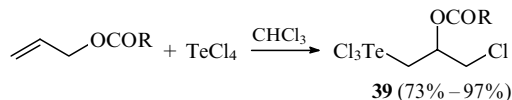
The reactions of allylic derivatives with TeCl_4 take different paths depending on the nature of the substituents at the *sp*³ carbon atom.¹⁰⁷ The reactions of TeCl_4 with allylic alcohols are generally accompanied by resinification of the reaction mixtures and the reaction products cannot be isolated. The reactions of TeCl_4 with allyl ethers occur according to the Markovnikoff rule giving rise to trichlorides **37** in yields above 80%.



The reaction of TeCl_4 with *N*-allylbenzamide,¹⁰⁷ like that with *N*-acetyldiallylamine,¹⁰⁸ afforded zwitterionic dihydrooxazolium salt **38**.



The addition of TeCl_4 to allyl carboxylates proceeded anomalously. In this case, 1,3-addition products, *viz.*, β -acyloxy- γ -chloropropyltellurium trichlorides **39**, rather than 1,2-addition products were obtained.¹⁰⁷

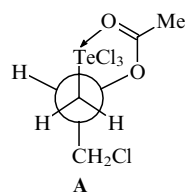


$\text{R} = \text{Me}, \text{Ph}, 4\text{-MeC}_6\text{H}_4, 4\text{-ClC}_6\text{H}_4, 4\text{-O}_2\text{NC}_6\text{H}_4, (E)\text{-CH}=\text{CHMe}, (E)\text{-CH}=\text{CHPh}.$

The reaction conditions depend on the nature of the substituent at the carbonyl carbon atom. Thus allyl benzoate and allyl 4-methylbenzoate reacted at room temperature, the reactions with allyl 4-chloro- and 4-nitrobenzoates proceeded only on boiling in chloroform, whereas allyl 2,4-dinitrophenylbenzoate did not react at all even on prolonged heating of the reaction mixture.

The reactions of TeCl_4 and TeBr_4 with allyl cinnamate in a mixture of Et_2O and H_2O at –30 °C occurred as 1,3-addition.¹⁰⁹

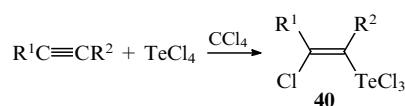
According to the data from IR and ¹H NMR spectroscopy,¹⁰⁷ compound **39** ($\text{R} = \text{Me}$) in solution adopts the conformation **A** in which the TeCl_3 group is located in the *gauche* position with respect to the acetoxy group. This conformation is stabilised through the intramolecular O–Te coordinate bond.



Tellurium tetrachloride reacts with α -methylallyl α,α -dimethylallyl and α -ethylallyl benzoates to give also 1,3-addition products.¹⁰⁹

b. Reactions of TeCl_4 with alkynes

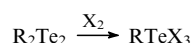
The reactions of TeCl_4 with alkynes have been studied to a substantially lesser extent than the reactions with alkenes. The reactions of TeCl_4 with alkynes in CCl_4 proceed regio- and stereospecifically giving rise to 2-chlorovinyltellurium chlorides **40** in yields of 75% and higher.^{54, 110, 111} The *Z* configuration of the compounds **40** was established by halodetelluration yielding (*Z*)-chlorobromo(iodo)alkenes (see Section III).¹¹¹

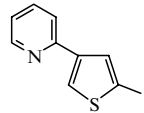
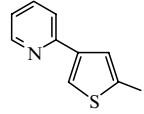


R ¹	R ²	Ref.
H	CH ₂ OH	111
Ph	H	54, 110, 111
Ph	Me	111
Ph	Et	111
Ph	Ph	110, 111

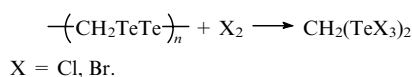
5. Oxidation of diorganyl ditellurides

A wide range of organytellurium trihalides were prepared by oxidation of diorganyl ditellurides with chlorine,^{22, 26, 91, 112–120} bromine,^{13, 26, 50, 51, 91, 113, 114, 116, 117, 120–131} iodine^{13, 51, 120, 121, 123, 127, 129–132} or fluorine diluted with an inert gas¹³³ at room or reduced temperature. Organytellurium trihalides can be prepared with the use of sulfonyl chloride^{112, 116} or thionyl chloride^{114, 115, 117, 120} instead of chlorine. These reactions are used primarily for the preparation of alkyltellurium trichlorides, aryltellurium tribromides and aryltellurium triiodides.

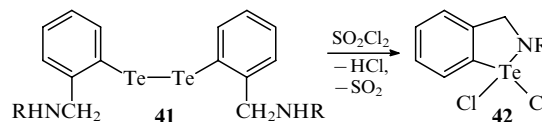


X	R	Ref.	X	R	Ref.
F	Ph	133	Br	4-MeOC ₆ H ₄	13, 50, 51, 123, 124, 127
Cl	Me	118	Br	4-EtOC ₆ H ₄	13, 51, 121, 123, 124, 127
Cl	Et	119	Br		13
Cl	HO ₂ CCH ₂	91	Br		129
Cl	3-FC ₆ H ₄	114	Br		128
Cl	4-FC ₆ H ₄	114	Br		26
Cl	Ph	112, 115	Br	2-PhCH ₂ C ₆ H ₄	13, 124, 127
Cl		120	Br	4-PhOC ₆ H ₄	13
Cl	2-OCHC ₆ H ₄	113	Br	4-PhSC ₆ H ₄	126, 131
Cl	2-NH ₂ -4-MeC ₆ H ₃	22	Br	4-PhC ₆ H ₄	130
Cl	2-NH ₂ -4-BrC ₆ H ₃	22	I	Me	130
Cl	2-NH ₂ -4-NO ₂ C ₆ H ₃	22	I	Et	130
Cl	2-PhCH ₂ C ₆ H ₄	26	I	Ph	127
Cl	2-Me ₂ NCH ₂ C ₆ H ₄	116	I	4-MeC ₆ H ₄	51, 127, 131
Cl	2-Me ₂ NCH(Me)C ₆ H ₄	117	I	4-MeOC ₆ H ₄	13, 51, 123, 127
Br	Me	122	I	4-EtOC ₆ H ₄	13, 51, 123, 127
Br	Et	130	I		13
Br	HO ₂ CCH ₂	91	I		129
Br	MeCH(CO ₂ H)	50	I	2-PhC ₆ H ₄	131, 132
Br	2-ClC ₆ H ₄	125	I	4-PhC ₆ H ₄	131
Br	3-FC ₆ H ₄	114	I	4-PhOC ₆ H ₄	13, 127
Br	4-FC ₆ H ₄	114, 125	I	4-PhSC ₆ H ₄	13
Br	Ph	124, 127			
Br	2-MeC ₆ H ₄	113, 125			
Br	4-MeC ₆ H ₄	51, 124, 127, 131			
Br		120			
Br	2-Me ₂ NCH ₂ C ₆ H ₄	116			
Br	2-Me ₂ NCH(Me)C ₆ H ₄	117			

Poly(ditellurides) are also oxidised with halogens. Thus treatment of poly(methylene ditelluride) with chlorine^{91, 93} or bromine⁹¹ afforded bis(trihalogenotellurio)methanes.

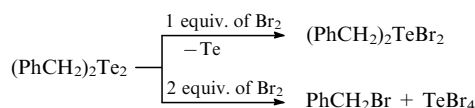


The reaction of bis{2-[N-(p-tolyl)benzylaminomethyl]phenyl} ditelluride (**41**) with SO₂Cl₂ yielded the telluracycle **42**.¹³⁴

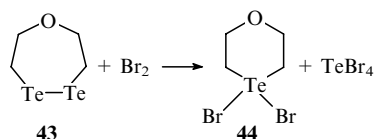


R = 4-MeC₆H₄.

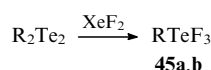
The behaviour of dibenzyl ditelluride in the reactions with halogens is anomalous compared to other ditellurides. Treatment of the former with bromine in CCl₄ led to the cleavage of both C–Te bonds giving rise to benzyl bromide and TeBr₄.¹³⁵ The reactions with the use of less than one equivalent of bromine afforded dibenzyltellurium dibromide as the major product.



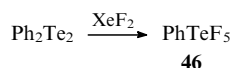
Ditelluride **43** also behaved anomalously. Thus the reaction with bromine yielded the telluracycle **44**.¹³⁶



Organytellurium trifluorides were synthesised not only with the use of fluorine but also using XeF₂ (see Refs 133, 137 and 138) or ClF.^{138, 139} Ditellurides containing perfluorinated organic groups were converted into organytellurium trifluorides **45** under the action of XeF₂,^{133, 138} whereas diphenyl ditelluride under the same conditions was converted into phenylpentafluorotellurium **46**.¹³⁷

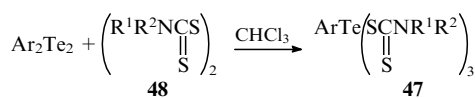


R = C₂F₅ (**a**), C₆F₅ (**b**).



The data on the reaction of bis(pentafluoroethyl) ditelluride with ClF are contradictory. Desjardins *et al.*¹³⁹ believed that the reaction afforded C₂F₅TeF₃ as the major product (*trans*-C₂F₅TeClF₄ and TeClF₅ were isolated as by-products in low yields), whereas Lau *et al.*¹³⁸ reported that a mixture of C₂F₅TeCl_xF_{3–x}, C₂F₅Cl and *trans*-C₂F₅TeClF₄ formed.

Some disulfides act as oxidising agents with respect to diaryl ditellurides. Thus thermochromic aryltellurium tris(dithiocarbamates) **47** were prepared by the reactions of diaryl ditellurides with thiuram disulfides **48** in almost quantitative yields.¹⁴⁰

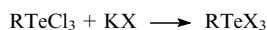


Ar = Ph, 4-MeOC₆H₄; R¹ = R² = Me, Et; R¹–R² = (CH₂)₅.

Oxidation of diaryl ditellurides with lead tetraacetate afforded the corresponding aryltellurium triacetates.^{141–143} The presence of these compounds in solutions was established by ¹H NMR spectroscopy. However, attempts to isolate these compounds were unsuccessful due to rapid hydrolysis.

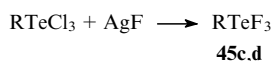
6. Exchange reactions of anionoid substituents

σ -Telluranes RTeX_3 containing different anionoid substituents can be synthesised with the use of organytellurium trichlorides in which the chlorine atoms are readily replaced by more nucleophilic anions X^- . Exchange reactions were used for the synthesis of a series of organytellurium tribromides^{61, 73, 74, 82} and organytellurium triiodides.^{13, 61, 73, 74, 82–95} Generally, exchange reactions are performed in aqueous-methanolic (ethanolic) solutions under the action of potassium halides.



X	R	Ref.	X	R	Ref.
Br, I	4-Me ₂ NC ₆ H ₄	61	Br, I	4-ClC ₆ H ₄ COCH ₂	82
Br, I	3-Me-4-HOC ₆ H ₃	73	I	4-HOC ₆ H ₄	13
Br, I	2-Cl-4-HOC ₆ H ₃	74			
Br, I	3-Cl-4-HOC ₆ H ₃	74	I		95
Br, I	2-HOC ₆ H ₄ COCH ₂	82			
Br, I	3-MeOC ₆ H ₄ COCH ₂	82			

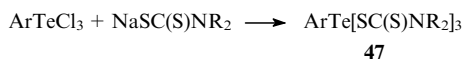
The exchange reactions were also used for the synthesis of aryltellurium trifluorides **45c,d**.⁵¹



R = 4-MeOC₆H₄ (**c**), 4-EtOC₆H₄ (**d**).

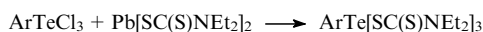
An analogous reaction was carried out with MeTeI_3 , but attempts to isolate the resulting MeTeF_3 in the pure form failed.¹⁴⁴

The exchange of chlorine atoms in organytellurium trichlorides is used as the major procedure for the synthesis of σ -telluranes RTeX_3 containing such substituents as $\text{SC}(\text{S})\text{NR}_2$ or $\text{SP}(\text{S})(\text{OR})_2$. Thus aryltris(thiocarbamoylthio)tellurium(IV) **47** was prepared by treatment of solutions of RTeCl_3 in CH_2Cl_2 , acetone or methanol with *N*-substituted sodium dithiocarbamates.^{116, 117, 140, 145, 146}



Ar = Ph, 4-MeOC₆H₄, 2-C₆H₄N=NPh, 2-Me₂NCH(Me)C₆H₄, 2-Me₂NCH₂C₆H₄; R = Me, Et, Bn.

The σ -telluranes **47** were also prepared by exchange reactions of aryltellurium trichlorides with $\text{Pb}[\text{SC}(\text{S})\text{NEt}_2]_2$ in dry benzene.¹⁴⁷

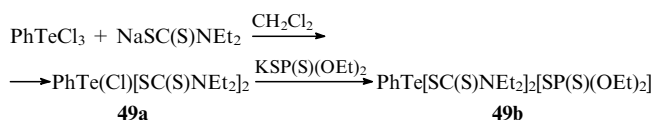


Ar = Ph, 4-MeOC₆H₄, 4-EtOC₆H₄, 3-Me-4-MeOC₆H₃.

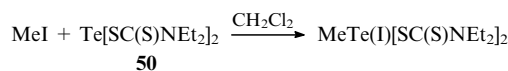
It should be noted that (according to the data from ¹²⁵Te NMR and Mössbauer spectroscopy¹⁴⁶) 2-(phenylazo)phenyltris(thiocarbamoylthio)tellurium(II) **47** (Ar = 2-C₆H₄N=N-C₆H₄-2) is very unstable and dissociates in solution to form 2-(phenylazo)phenylbis(thiocarbamoylthio)tellurium(II) and $[\text{R}_2\text{NC}(\text{S})\text{S}]_2$.

The evidence for the possible existence of mixed organytellurium trihalides of the RTeX_2Y type is contradictory (see Section II.7). However, compounds of this type were prepared upon treatment of aryltellurium trichlorides with sodium dialkyl-dithiocarbamates. Thus bis(*N,N*-diethylthiocarbamoylthio)-(chloro)phenyltellurium(IV) (**49a**) was synthesised in high yield starting from PhTeCl_3 and $\text{NaSC}(\text{S})\text{NEt}_2$.¹⁴⁸ Treatment of the compound **49a** with potassium *O,O*-diethyl dithiophosphate afforded the mixed σ -tellurane **49b** whose structure was established by X-ray diffraction analysis.¹⁴⁸

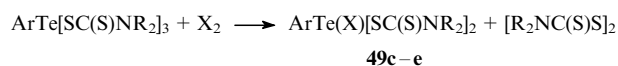
Mixed σ -telluranes of this type formed in the reactions of PhTeCl_3 with salts containing the $[\text{SC}(\text{S})\text{NEt}_2]^-$, $[\text{S}(\text{P})\text{S}(\text{OR})_2]^-$ or $[\text{SC}(\text{S})\text{OEt}]^-$ anions were studied in solutions by ¹³C, ³¹P and ¹²⁵Te NMR spectroscopy.¹⁴⁸



Yet another approach to the synthesis of the mixed derivatives **49** is based on oxidative addition of alkyl iodides to bis(*N,N*-diethylthiocarbamoylthio)tellurium(II) (**50**).¹⁴⁸

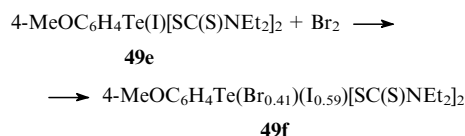


The mixed derivatives **49c–e** were also synthesised by the reactions of aryltris(*N,N*-dialkylthiocarbamoylthio)tellurium with halogens.^{149–151}

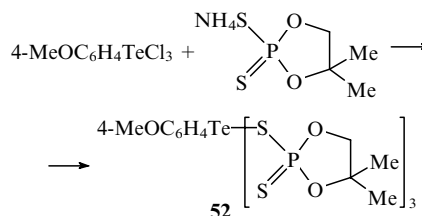
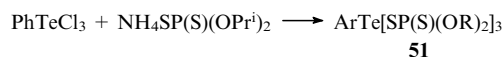


Compound 49	Ar	R	X	Ref.
c	Ph	Et	I	149
d	4-MeOC ₆ H ₄	Me	Br	150
e	4-MeOC ₆ H ₄	Et	I	151

It is noteworthy that the reaction of the compound **49e** with bromine was accompanied by partial replacement of the iodine atoms. The structure of the reaction product **49f** was established by X-ray diffraction analysis.¹⁵¹

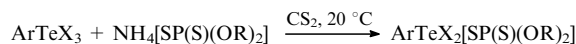


The exchange of the chlorine atoms in aryltellurium trichlorides was also used for the synthesis of aryltris(dialkoxythiophosphorylthio)tellurium (compounds **51** and **52**).¹⁵²



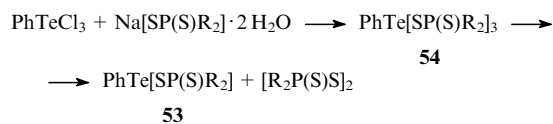
Compounds of the type **51** were prepared by the reactions of $\text{PhTe}(\text{OEt})_3$ (which has been prepared *in situ* from PhTeCl_3 and EtONa in EtOH) with *O,O*-dialkyl dithiophosphates, *e.g.*, $\text{HSP}(\text{S})(\text{OPr}^i)_3$.¹⁵²

As in the case of derivatives of dithiocarbamic acid, mixed derivatives can be synthesised.¹⁵³



Ar = Ph, 4-MeOC₆H₄; X = Br, Cl; R = Me, Et, Prⁱ.

Attempts to prepare σ -telluranes RTeX_3 containing $\text{SP}(\text{S})\text{R}_2$ ligands, unlike compounds containing $\text{SC}(\text{S})\text{NR}_2$ or $\text{SP}(\text{S})(\text{OR})_2$ ligands, were unsuccessful. The reaction of PhTeCl_3 with $\text{Na}[\text{SP}(\text{S})\text{R}_2]$ gave rise only to [diorganyl(thiophosphorylthio)]-phenyltellurium(II) **53** due apparently to decomposition of intermediate σ -telluranes of the type **54**.¹⁵⁴



7. Symmetrisation and reverse conversions

Symmetrisation and reverse conversions are well known, have been studied in detail for organic derivatives of Groups II–IV elements and are of preparative importance in the chemistry of organic derivatives of these elements. It was demonstrated¹¹⁵ that the symmetrisation reverse reaction also occurs in the case of diaryltellurium dichlorides.



R = OEt, OMe, H, Br.

Donor substituents favour these reactions. 4-Methoxy- and 4-ethoxyphenyltellurium trichlorides were prepared in 93% and 81% yields, respectively, upon refluxing (5 h) of equimolar mixtures of the reagents. Phenyl- and 4-bromophenyltellurium dichlorides were synthesised under more drastic conditions (a twofold excess of TeCl_4 and prolonged boiling).

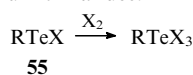
8. Miscellaneous procedures

In this section, we consider syntheses of σ -telluranes RTeX_3 , which are exemplified in a few compounds and are of no preparative importance.

Thus 4-hydroxy-3-methoxyphenyltellurium trichloride was prepared along with the corresponding dichloride by condensation of *o*-cresol with TeOCl_2 .¹⁵⁵ It was the only aryltellurium trichloride synthesised according to this procedure.

Organyltellurium trihalides were prepared by the reactions of some organotellurium compounds, viz., organyltellurenyl halides, organyl tellurocyanates, diorganyl tellurides and organyltellurinic acids, with halides (see Section II).

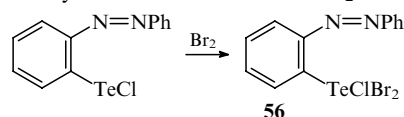
Oxidation of diorganyl ditellurides to form organyltellurium trihalides proceeds through intermediate formation of organyltellurenyl halides RTeX **55**.^{131, 156} Compounds of this type, which do not contain coordinating substituents, are unstable and readily undergo disproportionation to form R_2TeX_2 and Te .¹⁵⁷ Certain groups which can form strong intramolecular coordinate bonds with the Te atom through the N or O atoms stabilise the tellurenyl halides **55**. For example, the NO_2 , CHO, COR, $\text{CH}=\text{N}$, $\text{N}=\text{N}$ and CH_2NR_2 groups located at position 2 of the aryl or alkenyl substituent exert such a stabilising effect.^{158, 159} Compounds **55** can be synthesised not only by oxidation of ditellurides but also according to other procedures.¹⁶⁰ Hence, oxidation of the organyltellurenyl halides **55** was used for the preparation of organyltellurium trihalides.^{161–169}



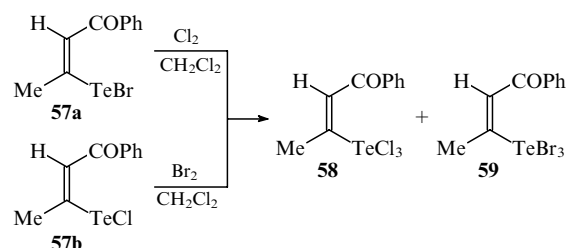
X	R	Ref.
Cl	2-PhCOC ₆ H ₄	164
Cl	2-C ₆ H ₄ CH=NC ₆ H ₄ Me-4	165–167
Cl	2-C ₆ H ₄ CH=NPh	166, 167
Cl	2-C ₆ H ₄ CH=NC ₆ H ₄ OMe-4	166, 167
Cl	(2-C ₆ H ₄ CH=NCH ₂) ₂	168
Cl	PhCOCH=CH	169
Cl	PhCOCH=CPh	169
Br	2-NO ₂ C ₆ H ₄	161
Br	2-HOCC ₆ H ₄	162
Br	2-PhCOC ₆ H ₄	163
Br	2-C ₆ H ₄ CH=NC ₆ H ₄ Me-4	165–167
Br	2-C ₆ H ₄ CH=NPh	166, 167
Br	2-C ₆ H ₄ CH=NC ₆ H ₄ OMe-4	166, 167
Br	2-C ₆ H ₄ CH=NC ₆ F ₅	166, 167
Br	(2-C ₆ H ₄ CH=NCH ₂) ₂	168
Br	PhCOCH=CH	169
Br	PhCOCH=CPh	169
I	2-C ₆ H ₄ CH=NC ₆ H ₄ Me-4	165–167
I	2-C ₆ H ₄ CH=NPh	166, 167
I	2-C ₆ H ₄ CH=NC ₆ H ₄ OMe-4	166, 167
I	2-C ₆ H ₄ CH=NC ₆ F ₅	166, 167

The oxidative addition is often performed with the use of SO_2Cl_2 instead of chlorine.^{165–167} Some tellurenyl iodides, for example, $\text{PhCOCH}=\text{C}(\text{Ph})\text{TeI}$, were not oxidised with iodine to form the corresponding triiodides.¹⁶⁹

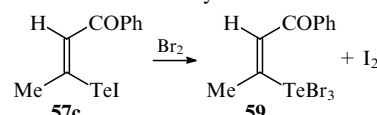
Aryltellurenyl chlorides can be used for the preparation of mixed aryltellurium trihalides ArTeX_2Y **56**.¹⁸



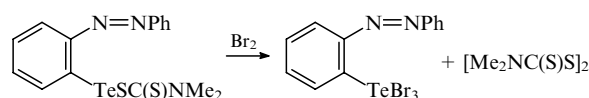
Attempts to synthesise compounds **56** starting from aryl 2-(halogenotellurenyl)vinyl ketones **57** were unsuccessful.¹⁶⁹ Thus the reaction of tellurenyl bromide **57a** with chlorine afforded a mixture of trichloride **58** and tribromide **59** in a ratio of 2:1. Treatment of tellurenyl chloride **57b** with bromine gave rise to a mixture of the same compounds, but the ratio was 1:2.¹⁶⁹



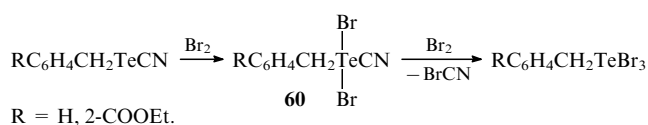
On the contrary, oxidative addition of bromine to tellurenyl iodide **57c** afforded vinyltellurium tribromide **59**.¹⁶⁹



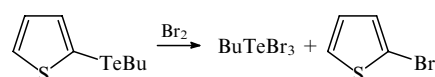
2-(*N,N*-Dimethylthiocarbamoyltellurenyl)azobenzene reacted analogously.¹⁴⁶



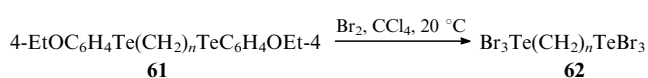
The reactions of benzyl tellurocyanates with two equivalents of bromine were accompanied by the cleavage of the $\text{Te}-\text{CN}$ bond yielding the corresponding benzyltellurium tribromides.^{170, 171} Apparently, σ -telluranes **60** were formed in these reactions as intermediates.¹⁷⁰



It is known^{3, 4, 6, 7} that diorganyl tellurides R_2Te react with halogens to form diorganyltellurium dihalides R_2TeX_2 . However, the reactions of some diorganyl tellurides with halogens proceed with the cleavage of one of the $\text{C}-\text{Te}$ bonds giving rise to the corresponding organyltellurium trihalides. Thus butyltellurium tribromide was obtained from butyl-2-thienyl telluride.¹⁷²

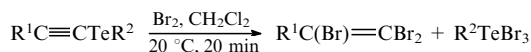


Compounds **61** underwent scission under the action of bromine in CCl_4 to form α,ω -bis(tribromotellurio)alkanes **62**.¹⁷³



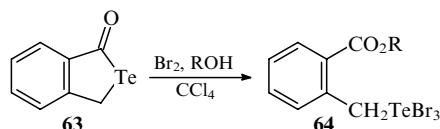
$n = 6$ (42%), 10 (40%).

Tellurium-substituted alkynes add bromine with simultaneous elimination of organytellurium tribromide.¹⁷⁴



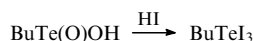
$\text{R}^1 = \text{Ph}, \text{C}_5\text{H}_{11}, 4\text{-BrC}_6\text{H}_4, \text{R}^2 = \text{Bu}; \text{R}^1 = \text{Ph}, \text{R}^2 = 4\text{-MeOC}_6\text{H}_4.$

The C—Te bond was cleaved in the reaction of telluraphthalide **63** with bromine.¹⁷¹ In the presence of alcohols, the reaction afforded 2-alkoxycarbonylbenzyltellurium tribromides **64**.¹⁷¹



$\text{R} = \text{Me}, \text{Et}.$

In the reactions with HI, tellurinic acids are converted into organytellurium triiodides. Thus tellurinic acid as a component of the complexes $\text{Bu}_2\text{TeO} \cdot 3\text{BuTe}(\text{O})\text{OH}$ and $2(\text{Bu}_2\text{TeO}) \cdot \text{BuTe}(\text{O})\text{OH}$, which have been prepared by oxidation of dibutyl telluride, was converted into butyltellurium triiodide under the action of HI.¹⁷⁵



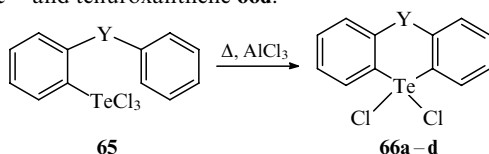
III. Reactions of σ -telluranes RTeX_3

The reactions of σ -telluranes RTeX_3 were studied primarily for organytellurium trichlorides. Some of them proceed with retention of the coordination number of the tellurium atom.[†]

1. Transformations of σ -telluranes RTeX_3 into σ -telluranes R_2TeX_2

Transformations of σ -telluranes RTeX_3 into compounds R_2TeX_2 proceed with retention of the coordination number of the tellurium atom, but are accompanied by the formation of an additional C—Te bond. These reactions are of preparative importance in the synthesis of σ -telluranes $\text{R}^1\text{R}^2\text{TeCl}_2$ (for earlier data, see Refs 3, 4, 6 and 7). Since aryltellurium trichlorides exhibit electrophilic properties, they enter into reactions analogous to those of TeCl_4 . Thus these compounds react with different heteroorganic compounds to form symmetrical and non-symmetrical organytellurium dichlorides $\text{R}^1\text{R}^2\text{TeCl}_2$, are involved in electrophilic substitution with activated arenes to give diaryltellurium dichlorides $\text{Ar}^1\text{Ar}^2\text{TeCl}_2$, react with compounds containing the activated methylene group to form σ -telluranes ($\text{ArTeCl}_2\text{CH}_2\text{COR}$ in the case of ketones) and add to double and triple bonds yielding derivatives of the types $\text{ArTeCl}_2\text{CH}(\text{R}^1)\text{CH}(\text{Cl})\text{R}^2$ and $\text{ArTeCl}_2\text{C}(\text{R}^1)=\text{C}(\text{Cl})\text{R}^2$, respectively. However, aryltellurium trichlorides are weaker electrophilic agents than TeCl_4 , and hence, the above-mentioned reactions proceed under more drastic conditions.

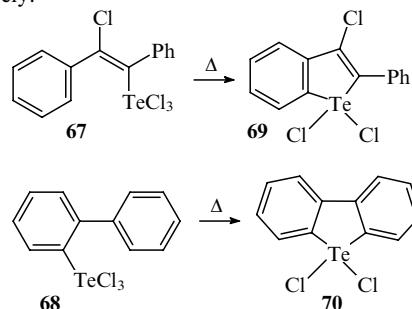
Intramolecular cyclisation of aryl- and arylvinyltellurium trichlorides giving rise to different six- and five-membered tellurium-containing heterocycles is of particular interest.¹⁷⁶ Thus thermal or AlCl_3 -catalysed cyclisation of aryltellurium trichlorides **65** afforded tetracoordinate tellurium derivatives, viz., phenoxatellurine **66a**,⁵⁶ thiophenoxatellurine **66b**,¹³ phenotellurazine **66c**²⁰ and telluroxanthene **66d**.²⁶



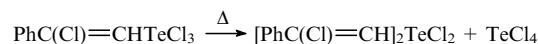
$\text{Y} = \text{O} \text{ (a)}, \text{S} \text{ (b)}, \text{NH} \text{ (c)}, \text{CH}_2 \text{ (d)}.$

[†] Exchange reactions of anionoid substituents are considered in Section II.6.

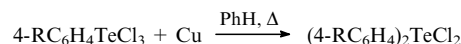
Heating of organytellurium trichlorides **67** and **68** at high temperature gave rise to 1,1,3-trichloro-2-phenylbenzo[*b*]tellurophene (**69**)¹⁷⁷ and 1,1-dichlorodibenzotellurophene (**70**),⁸ respectively.



Aryltellurium trichlorides and vinyltellurium trichlorides can be converted into the corresponding dichlorides by symmetrisation. Thus heating of solutions of 2-chloro-2-phenylvinyltellurium chloride in EtOH or AcOH resulted in elimination of the TeCl_4 molecule.¹¹⁰

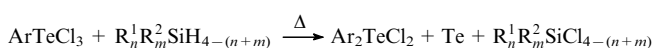


Aryltellurium trichlorides do not undergo spontaneous symmetrisation. These compounds were converted into diaryltellurium dichlorides only upon boiling of their solutions in benzene in the presence of a copper powder (the yields were 60%–70%).¹¹⁵



$\text{R} = \text{OMe}, \text{OEt}.$

Aryltellurium trichlorides were converted into diaryltellurium dichlorides also under the action of organylsilicon hydrides.¹⁷⁸ Aryltellurium trichlorides reacted with silicon hydrides (in a ratio of 3:4) with stirring at room temperature for 6–8 h to afford diaryl ditellurides. When refluxed for 6–10 h, the mixture of the reagents taken in a ratio of 1:2 gave rise to diaryltellurium dichlorides in 75%–95% yields.



$\text{Ar} = \text{Ph}, 4\text{-MeOC}_6\text{H}_4, 4\text{-EtOC}_6\text{H}_4; \text{R}^1, \text{R}^2 = \text{Ph}, \text{C}_6\text{H}_{13}, \text{Me}; n = 1, 2; m = 1, 2.$

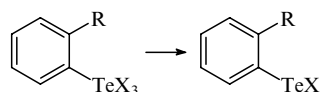
Certain reactions of σ -telluranes RTeX_3 are accompanied by a decrease in the coordination number of the Te atom to 2 (reduction) or 3 (hydrolysis).

2. Reduction of aryltellurium trihalides to aryltellurenyl halides[‡]

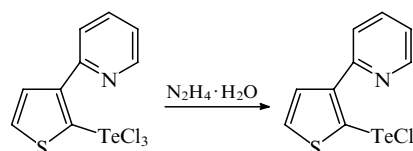
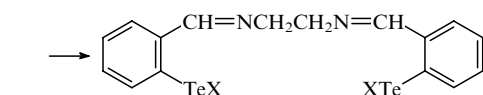
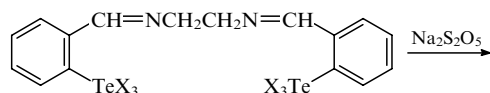
Reduction of aryltellurium trichlorides affords different products depending on the structure of the organic ligands. Aryltellurium trihalides containing coordinating substituents in the *ortho* position are reduced to aryltellurenyl halides, whereas organytellurium trihalides in which such substituents are absent are reduced only to diorganyl ditellurides.

Aryltellurium trihalides containing $\text{CH}=\text{N}$,^{23,24,120,168} $\text{N}=\text{N}$,¹⁸ NO_2 ,¹⁶¹ CH_2NMe_2 (see Ref. 116) or $\text{CH}(\text{Me})\text{NMe}_2$ (see Ref. 117) groups in the *ortho* position were reduced to aryltellurenyl halides. Hydrazine hydrate^{23,24,116,117,120} NaBH_4 ,¹⁸ NaHSO_3 (see Ref. 161) and $\text{Na}_2\text{S}_2\text{O}_5$ (see Ref. 168) were used as reducing agents.

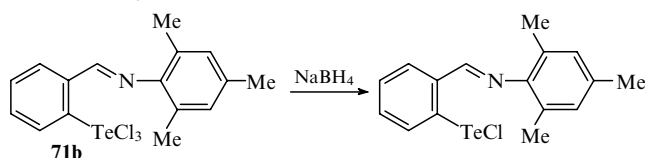
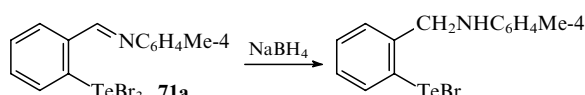
[‡] Reduction of organytellurium trihalides to ditellurides is not considered in the present review because these reactions have been surveyed in detail in a recent review.¹⁷⁹



R	Reducing agent	Ref.
	N ₂ H ₄ · H ₂ O	23, 24
	N ₂ H ₄ · H ₂ O	24
N = NPh	NaBH ₄	18
NO ₂	NaHSO ₃	161
CH ₂ NMe ₂	N ₂ H ₄ · H ₂ O	116
CH(Me)NMe ₂	N ₂ H ₄ · H ₂ O	117

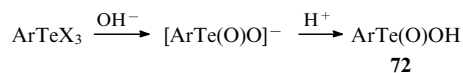


In the case of *N*-(2-tribromotelluriobenzylidene)-4-methylaniline (**71a**), both the TeBr₃ and azomethine groups were reduced under the action of sodium borohydride,¹³⁴ whereas the azomethine group in sterically hindered *N*-(2-trichlorotelluriobenzylidene)-2,4,6-trimethylaniline (**71b**) remained unchanged.



3. Hydrolysis of organytellurium trihalides

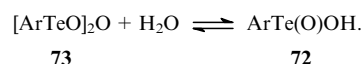
Alkaline hydrolysis of aryltellurium trihalides followed by acidification of the reaction mixture afforded aryltellurinic acids **72** in 70%–100% yields.



X = Cl, Br.

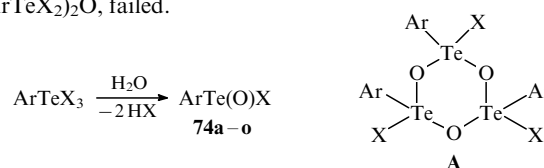
Ar	Ref.	Ar	Ref.
Ph	180	4-BuOC ₆ H ₄	182
2-MeC ₆ H ₄	113	4-PhOC ₆ H ₄	180, 182
4-HOC ₆ H ₄	46, 180	2-HOCC ₆ H ₄	113
4-EtOC ₆ H ₄	46, 180, 181		129, 180, 182
4-MeOC ₆ H ₄	46, 180, 182		

In some cases, acidification gives rise to anhydrides **73** rather than to tellurinic acids **72** due apparently to the existence of the following equilibrium in solution



Presumably, this equilibrium is shifted to the right only in a strongly acidic medium. In the presence of weak acids (for example, AcOH), the anhydrides **73** were formed as the final hydrolysis products of aryltellurium trihalides.^{129, 180–182}

Aryltellurium trichlorides and tribromides undergo partial hydrolysis under the action of cold water to form aryltellurium oxohalides **74**.^{46, 63, 180, 181, 183} Aryltellurium triiodides are inert to cold water. In most cases, hydrolysis at high temperature afforded unidentified compounds. Poor solubility of aryltellurium oxohalides in ordinary organic solvents was attributed¹⁸¹ to the fact that they have a trimeric structure **A**. Attempts to isolate possible intermediate products of partial hydrolysis, viz., compounds (ArTeX₂)₂O, failed.



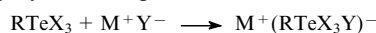
Compound 74	X	R	Ref.
a	Cl	Ph	180
b	Cl	4-HOC ₆ H ₄	46
c	Cl	4-MeOC ₆ H ₄	46, 180, 183
d	Cl	4-EtOC ₆ H ₄	46, 180, 181, 183
e	Cl	3,4-(MeO) ₂ C ₆ H ₃	183
f	Cl	4-PhOC ₆ H ₄	180
g	Cl		180
h	Cl		63
i	Cl		63
j	Cl		63
k	Br	Ph	180, 181
l	Br	4-MeOC ₆ H ₄	180
m	Br	4-EtOC ₆ H ₄	180, 181
n	Br	4-PhOC ₆ H ₄	180
o	Br		180

Aryltellurium oxochlorides **74a,c,d** were also synthesised by treatment of the corresponding aryltellurium trihalides with 2-phenyliodonobenzoate monohydrate.¹⁸⁴

Alkyltellurium oxohalides RTe(O)X (R = Me and X = Cl, Br or I; R = Et and X = I)¹⁸⁵ and anhydrides [RTe(O)]₂O (R = C₈H₁₇, C₁₀H₂₁ or C₁₂H₂₅)¹⁸⁶ were prepared according to a procedure analogous to that used for the synthesis of the aryl analogues **74a–o**. Acidification of an aqueous solution of the salt [Me₃Te]⁺[MeTe(O)O][–] afforded a mixture of methyltellurinic acid and its anhydride.¹⁸⁷

4. Synthesis of salts containing organyltetrahalogenotellurate anions

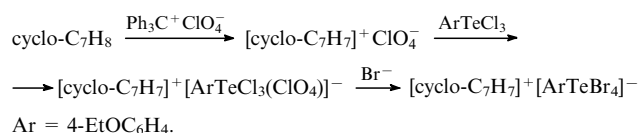
Reactions yielding salts containing organyltetrahalogenotellurate anions and complexation reactions are accompanied by an increase in the coordination number of the tellurium atom. The reactions of different organytellurium trihalides with onium salts in organic solvents (MeOH or CHCl₃) give rise to salts containing organyltetrahalogenotellurate anions.^{181, 187–192}



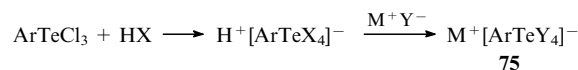
75

R	X	Y	M	Ref.
Me	I	Br	Me ₃ Te	187
Me	Br	Br	Me ₃ Te	187
Me	Br	I	Me ₃ Te	187
Me	Cl	Br	Et ₄ N	188
Ph	Cl	Cl	Et ₄ N	189
Ph	Cl	Cl	Ph ₃ PCH ₂ Ph	190
Ph	Cl	Cl	Ph ₄ P	190
Ph	Cl	Cl	Ph ₄ As	181, 189
Ph	Cl	Cl	Ph ₃ Se	189
Ph	Cl	Cl	Ph ₂ I	189
Ph	Cl	Cl	C ₅ H ₅ NH	181
Ph	Cl	Br	Ph ₃ PMe	190
Ph	Cl	Br	Ph ₃ PCH ₂ CO ₂ Et	190
Ph	Cl	Br	Ph ₃ Te	190
Ph	Cl	Br	cyclo-C ₇ H ₇	190
Ph	Cl	I	Bu ₄ N	191
Ph	Br	Br	Me ₄ N	189
Ph	Br	Br	Et ₄ N	189
Ph	Br	Br	Ph ₃ PMe	190
Ph	Br	Br	Ph ₄ P	190
Ph	Br	Br	Ph ₃ PCH ₂ CO ₂ Et	190
Ph	Br	Br	Ph ₃ S	189
Ph	Br	Br	Ph ₂ I	189
Ph	Br	Br	cyclo-C ₇ H ₇	190
Ph	I	I	Pr ₄ N	189
Ph	I	I	Me ₃ S	189
Ph	I	Cl	Ph ₃ PCH ₂ Ph	190
Ph	I	Br	cyclo-C ₇ H ₇	190
4-EtOC ₆ H ₄	Cl	Cl	Me ₄ N	189
4-EtOC ₆ H ₄	Cl	Cl	C ₅ H ₅ NH	181
4-EtOC ₆ H ₄	Cl	Cl	Ph ₃ PCH ₂ Ph	190
4-EtOC ₆ H ₄	Cl	Cl	Ph ₄ P	190
4-EtOC ₆ H ₄	Cl	Cl	Ph ₄ As	189
4-EtOC ₆ H ₄	Cl	Cl	Ph ₃ Se	189
4-EtOC ₆ H ₄	Cl	Cl	Ph ₂ I	189
4-EtOC ₆ H ₄	Cl	Br	Ph ₃ P	190
4-EtOC ₆ H ₄	Cl	Br	Ph ₃ PCH ₂ CO ₂ Et	190
4-EtOC ₆ H ₄	Cl	Br	cyclo-C ₇ H ₇	190
4-EtOC ₆ H ₄	Br	Br	Et ₄ N	189
4-EtOC ₆ H ₄	Br	Br	Ph ₃ PMe	189
4-EtOC ₆ H ₄	Br	Br	Ph ₃ PCH ₂ CO ₂ Et	189
4-EtOC ₆ H ₄	Br	Br	Ph ₄ P	189
4-EtOC ₆ H ₄	Br	Br	Ph ₃ S	189
4-EtOC ₆ H ₄	Br	Br	Ph ₂ I	189
4-EtOC ₆ H ₄	Br	Br	cyclo-C ₇ H ₇	190
4-EtOC ₆ H ₄	Br	Cl	Ph ₃ PCH ₂ Ph	190
4-EtOC ₆ H ₄	I	I	Pr ₄ N	189
4-EtOC ₆ H ₄	I	I	Me ₃ S	189
4-EtOC ₆ H ₄	I	Cl	Ph ₃ PCH ₂ Ph	190
4-EtOC ₆ H ₄	I	Br	cyclo-C ₇ H ₇	190
4-PhOC ₆ H ₄	Cl	Cl	Et ₂ NH ₂	192

Tropylium 4-ethoxyphenyltetra bromotellurate was prepared by the reaction of the corresponding aryltellurium trichloride with tropylium perchlorate followed by anion exchange.¹⁹⁰



The reactions of aryltellurium trihalides with onium salts in aqueous solutions of hydrohalic acids also gave rise to salts **75** in high yields.^{189, 190}



Ar = Ph, 4-EtOC₆H₄; X = Cl, Br; M = cyclo-C₇H₇, Ph₃PMe, Ph₃PCH₂CO₂Et.

5. Complexation

σ-Telluranes RTeX₃ act as Lewis acids in complexation. In contrast to tellurium tetrahalides which typically form 2:1 adducts,¹⁹³ organytellurium trihalides give rise mainly to 1:1 complexes.

Aryltellurium trichlorides ArTeCl₃ (Ar = Ph, 4-MeC₆H₄, 4-MeOC₆H₄, 4-EtOC₆H₄ or 4-PhOC₆H₄)^{125–128} form 1:1 complexes with pyridine, picolines,^{125–128} pyridine *N*-oxide and picoline *N*-oxide.^{194–197} In solution in nitromethane, the complexes with pyridine and picolines act as electrolytes (1:1) and have, apparently, the structure [ArTeCl₂·L]⁺Cl[−].¹⁹⁴ The complexes with *N*-oxides are weak electrolytes of the formula ArTeCl₃·L.¹⁹⁴

In addition to the complexes with the above-mentioned ligands, complexes of aryltellurium trichlorides with a number of other nitrogen-, phosphorus- and oxygen-containing bases, *viz.*, with trimethyl(ethyl)amine,^{195–197} α-naphthylamine,¹⁹⁵ ethylene diamine,¹⁹⁵ benzimidazole,^{195–197} benzothiazole,^{195, 196} 2,2'-bipyridyl,^{195, 197} 1,10-phenanthroline,^{196, 197} triphenylphosphine,¹⁹⁵ triphenylphosphine oxide,^{195–197} triphenylphosphine sulfide,¹⁹⁵ triphenylarsine oxide^{195–197} and dimethyl sulfoxide,^{195–197} were isolated in the individual state as 1:1 complexes. The composition and the enthalpy of formation of the complex of PhTeCl₃ with (C₆H₁₃)₂SO were determined by calorimetric titration.¹⁹⁸ Judging from the enthalpies of formation, the acceptor abilities of tetracoordinate tellurium derivatives decrease in the series TeCl₄ > PhTeCl₃ > Ph₂TeCl₂.¹⁹⁸

It should be noted that Garad¹⁹⁹ assigned the 1:1 and 2:1 compositions to complexes of aryltellurium trichlorides with bidentate ligands (bipyridyl or phenanthroline) and monodentate ligands [pyridine, pyridine *N*-oxide or (C₈H₁₇)₃P=O], respectively, contrary to the above-considered data.^{194–197}

Organytellurium trihalides exhibit acceptor properties also with respect to sulfur-containing donors. It was demonstrated²⁰⁰ that organytellurium trihalides 4-EtOC₆H₄TeX₃ (X = Cl, Br or I), like tellurium tetrahalides, react with tetramethylthiuram disulfide. These reactions are accompanied by extrusion of one sulfur atom to form 2:1 complexes of aryltellurium trihalides with tetramethylthiuram sulfide.

According to IR and ¹H NMR spectral data, the 1:1 complexes of RTeCl₃ and RTeBr₃ (R = Me, Et, 4-MeOC₆H₄ or 4-EtOC₆H₄) with tetramethylthiourea^{130, 195, 201} have a square-pyramidal structure with the organic substituents in apical positions. Three halogen atoms and the *S*-coordinated ligand are located in the base of the pyramid.^{130, 201} The reactions of phenyltellurium trihalides with thiourea in aqueous-methanolic solutions were accompanied by reduction of Te(IV) to form the complexes PhTeX·(NH₂)₂CS.²⁰²

Tetramethyl-¹²⁴ and tetraethyldithiooxamides¹²³ belong to yet another type of sulfur-containing ligands giving the 1:1 complexes ArTeX₃·C(S)(NR₂)C(S)(NR₂) (R = Me or Et) with aryltellurium trihalides 4-RC₆H₄TeX₃ (R = H, Me, MeO, EtO, PhO or PhS; X = Cl, Br or I). The long-wavelength IR spectra and Raman spectra provide evidence in favour of the octahedral

structure of the complexes containing bidentate ligands coordinated through the sulfur atoms of the thiocarbonyl groups.

Measurements of the dipole moments (in benzene) demonstrated that aryltellurium trichlorides form 1:1 complexes with donors of the $\text{Ph}_3\text{P}=\text{X}$ (X is a lone electron pair, O, S or Se) and $\text{PhP}(\text{O})\text{Me}_2$ types.²⁰³ The dipole moments are indicative of the donor-acceptor character of the bond between the components of the complexes. The coordination centres of the complexes adopt a pseudooctahedral configuration in which the donor is located in the *cis* position with respect to the lone electron pair of the tellurium atom and in the *trans* position with respect to the chlorine atom. It is noteworthy that the reactions of 4- $\text{RC}_6\text{H}_4\text{TeCl}_3$ (R = H, OH or OMe) with thiosemicarbazones of benzaldehyde, acetophenone, salicylaldehyde and 2-hydroxyacetophenone afforded ionic tricoordinate Te(II) complexes $[\text{ArTe}(\text{TSK})_2]^+\text{Cl}^-$ (TSK is the corresponding thiosemicarbazone) in which the Te atom is coordinated through the sulfur atom.²⁰⁴

In the reactions with strong Lewis acids, *e.g.*, with SbCl_5 , organytellurium trichlorides RTeCl_3 (R = Me, Et or 4- MeOC_6H_4) act as donors to give 1:1 complexes.¹¹⁹ Ionic structures were assigned to the complexes $[\text{RTeCl}_2]^+\text{SbCl}_6^-$ based on the facts that their IR spectra are similar to those of the ionic complexes $\text{RSeCl}_3 \cdot \text{AlCl}_3$ and have bands characteristic of the SbCl_6^- ion.

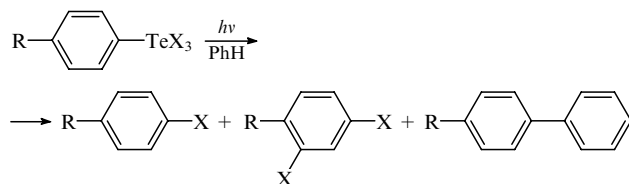
The enthalpies of formation of complexes of tetracoordinate tellurium derivatives with AlBr_3 (1:1 composition)¹⁹⁸ are indicative of an increase in the donating ability of the tellurium atom in the series $\text{TeCl}_4 < \text{PhTeCl}_3 < \text{Ph}_2\text{TeCl}_2$.

6. Detelluration

Elimination of tellurium (detelluration) is also characteristic of σ -telluranes RTeX_3 . Some of these reactions are of particular preparative interest. Detelluration is performed by pyrolysis, photolysis or under the action of Raney nickel, Pd(II) salts, oxidants or some nucleophilic reagents.

Heating of 2-chloroethyl-⁹⁷ or 2-chloropropyltellurium trichlorides⁹⁶ afforded Te, HCl, saturated (isopropyl chloride) and unsaturated (vinyl chloride and allyl chloride) halogen-containing derivatives and 1,2-dichloroalkanes. Pyrolysis of 2-chlorocyclohexyltellurium trichloride gave rise to cyclohexyl chloride, hexene and benzene along with Te and HCl.⁹⁶

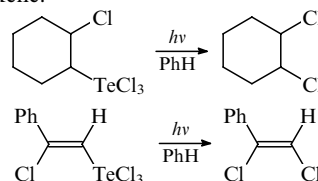
Photolysis of organytellurium trihalides proceeds in a different way.^{101,205} Irradiation of solutions of these compounds in benzene afforded organic halogen-containing derivatives, the halogen atoms occupying positions to which the tellurium-containing group was initially bound (*ipso* substitution).



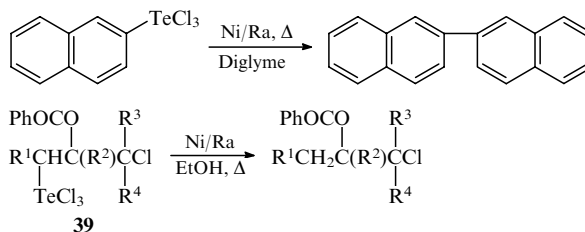
R = MeO, Me, H; X = Cl, Br, OAc.

Thus irradiation of a solution of 4-methoxyphenyltellurium trichloride in C_6H_6 using a high-pressure mercury lamp at 20–30 °C for 1 h afforded 4-chloroanisole in 70% yield and 2,4-dichloroanisole as a by-product (20%). Photolysis of 4-methoxyphenyltellurium tribromide gave rise to 4-bromoanisole in 30% yield. Irradiation of a solution of 4-methoxyphenyltellurium triacetate [prepared *in situ* from Ph_2Te_2 and $\text{Pb}(\text{OAc})_4$ in AcOH] afforded 4-acetoxyanisole in 14% yield. In some cases, coupling products of organic radicals of σ -telluranes with benzene were also obtained in trace amounts.^{101,205} The yields of aryl halides decrease as the donor properties of substituents in the aryl groups of σ -telluranes decrease.

The reactions of cycloalkyl- and vinyltellurium trichlorides proceed analogously.^{101,205} In the latter case, the reaction proceeds with retention of the geometric configuration of the initial alkene.

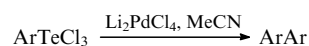


Aryltellurium trichlorides undergo detelluration upon heating with Raney nickel (Ni/Ra) in diglyme to form biaryls.⁷¹ Apparently, this reaction proceeds through initial reduction of tellurium trichlorides to form ditellurides followed by elimination of tellurium.¹⁰⁷ Detelluration of (β -acyloxy- γ -chloroalkyl)tellurium trichlorides of the type **39** under the action of Raney nickel gave rise to chlorohydrin esters in 26%–78% yields.¹⁰⁷

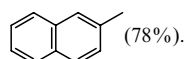


R ¹	R ²	R ³	R ⁴
H	H	H	H
Me	H	H	H
H	Me	H	H
H	H	Me	H
H	H	Me	Me

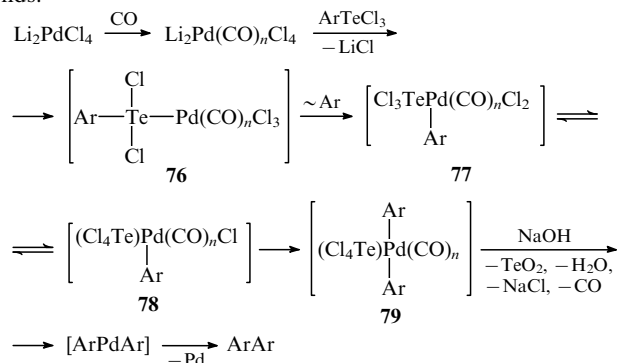
Biaryls were also formed upon treatment of aryltellurium trichlorides with PdCl_2 and NaOAc in AcOH⁴⁹ or with Li_2PdCl_4 in MeCN.²⁰⁶ The latter reagent is more efficient than the former. The formation of biaryls is favoured by the presence of donor substituents in the aryl groups.



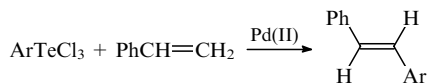
Ar = 4- MeOC_6H_4 (54%), 4- BuOC_6H_4 (26%), 4- PhOC_6H_4 (29%),



The reactions performed under a CO atmosphere afforded biaryls in approximately the same yields, but the reaction rates were substantially higher.²⁰⁶ However, good yields of biaryls were achieved only after treatment of the reaction mixture with a solution of NaOH. In the latter case, carboxylic acids were obtained as by-products. The reactions were accelerated due to the formation of active intermediates **76**–**79** containing Pd–CO bonds.²⁰⁶

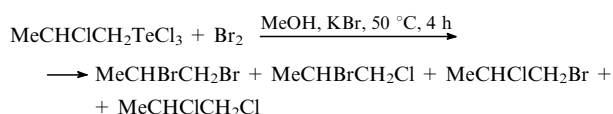


Treatment of a mixture of aryltellurium trichlorides, PdCl_2 and NaOAc in AcOH with a tenfold excess of styrene afforded *trans*-stilbenes in rather low yields (7%–38%) along with trace amounts of biaryls.⁴⁹ It should be noted that the yields of stilbenes in the reactions with aryltellurium trichlorides are lower than those obtained in the reactions with diaryltellurium dichlorides containing the same substituents.

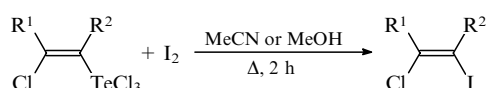


$\text{Ar} = \text{Ph}, 4\text{-MeC}_6\text{H}_4, 4\text{-MeOC}_6\text{H}_4$.

Detelluration of different types of organytellurium trihalides proceeds also under the action of halogens giving rise to the corresponding organyl halides (halodetelluration).^{96, 111, 207} Apparently, halodetelluration was observed for the first time in the treatment of 2-chloropropyltellurium trichloride with bromine.⁹⁶



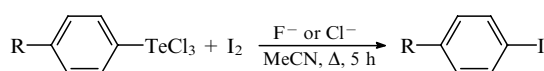
Iododetelluration of (*Z*)-2-chlorovinyltellurium trichlorides proceeded with retention of the configuration of the initial alkenes giving rise to (*Z*)-chloroiodoalkenes in 40%–94% yields.¹¹¹



$\text{R}^1 = \text{Ph}, \text{R}^2 = \text{H, Me, Et, Ph}; \text{R}^1 = \text{CH}_2\text{OH}, \text{R}^2 = \text{H}$.

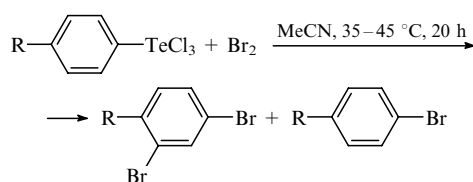
Bromodetelluration occurs only upon treatment of vinyltellurium trichlorides with *N*-bromosuccinimide in the presence of AlCl_3 .¹¹¹

Iododetelluration of aryltellurium trichlorides containing donor substituents under the action of iodine proceeded efficiently only in the presence of potassium fluoride, cesium fluoride, ammonium fluoride, mercury(II) chloride or SbCl_5 to form aryl iodides in yields higher than 80%.²⁰⁷ However, the reactions of phenyl- and 4-bromophenyltellurium trichlorides with iodine under identical conditions gave rise to aryl iodides in very low yields. This fact is indicative of the electrophilic character of the reaction.²⁰⁷ Apparently, the catalytic action of fluoride ions is associated with the formation of the intermediates $[\text{ArTeCl}_3\text{F}_2]^-$ due to which the electron density at the tellurium atom and at the C–Te bond increases, which favours the electrophilic attack of the halogen. The function of metal chlorides is to activate iodine by complexation or *in situ* formation of more reactive iodine monochloride.²⁰⁷



$\text{R} = \text{Me, OMe}$.

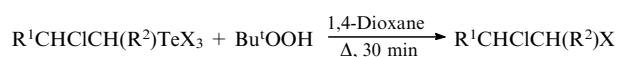
Bromodetelluration of aryltellurium trichlorides with bromine in MeCN , 1,4-dioxane or CCl_4 gave rise to 2,4-dibromoarenes in rather high yields, while 4-bromoarenes were obtained in trace amounts.²⁰⁷ The selective formation of dibromides was attributed to bromination of the initial 4-bromoarenes catalysed by organic derivatives of tellurium(IV).²⁰⁷



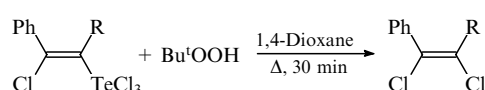
$\text{R} = \text{H, Me, OMe}$.

Chlorodetelluration of aryltellurium trichlorides under the action of different chlorinating agents (Cl_2 , SbCl_5 or Bu^tOCl) proceeded with very low yields even in the case of highly reactive 4-methoxyphenyltellurium trichloride.²⁰⁷ Cyanodetelluration of 4-methoxyphenyltellurium trichloride with CuCN in DMF also occurred in very low yield (5%).²⁰⁷

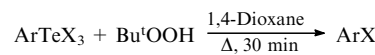
Halodetelluration of organytellurium trichlorides proceeded rather readily under the action of *tert*-butyl hydroperoxide.^{101, 208} Different types of organytellurium trihalides, *viz.*, with 2-chloro-alkyl-, 2-chlorocyclohexyl-, alkenyl- and aryltellurium trihalides, enter into this reaction. In most of reactions with alkenyl derivatives, the initial configuration is retained.¹⁰¹ The yields of alkenyl halides are lower than those of alkyl and aryl halides. It was thus assumed¹⁰¹ that the reactivities of organytellurium trihalides in oxidative detelluration change in the order: alkyl > aryl > alkenyl.



$\text{R}^1 = \text{C}_8\text{H}_{17}, \text{PhCH}_2; \text{R}^2 = \text{H}; \text{R}^1 - \text{R}^2 = (\text{CH}_2)_4; \text{X} = \text{Cl, I}$.

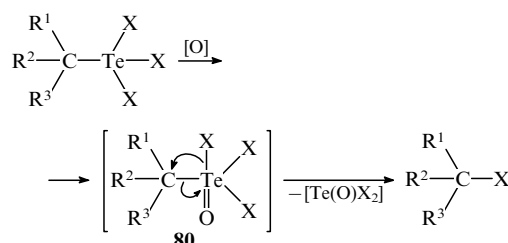


$\text{R} = \text{H, Ph}$.

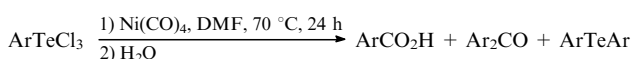


$\text{Ar} = 4\text{-MeC}_6\text{H}_4, 4\text{-MeOC}_6\text{H}_4, \text{1-naphthyl}, \text{2-naphthyl}; \text{X} = \text{Cl, Br}$.

The possible reaction mechanism involving the formation of unstable organic derivatives of tellurium(VI) **80** is shown in the scheme.¹⁰¹

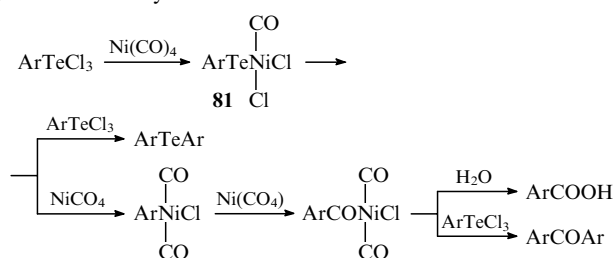


The reactions of aryltellurium trichlorides with $\text{Ni}(\text{CO})_4$ in DMF resulted in detelluration. Subsequent treatment of the reaction mixtures with water afforded carboxylic acids in 35%–51% yields.²⁰⁹ Symmetrical ketones and diaryl tellurides were obtained as by-products (sometimes in yields of up to 15%). The reaction of 4-methoxyphenyltellurium trichloride with $\text{Fe}_2(\text{CO})_9$ yielded bis(4-methoxyphenyl) telluride as the only product.²⁰⁹

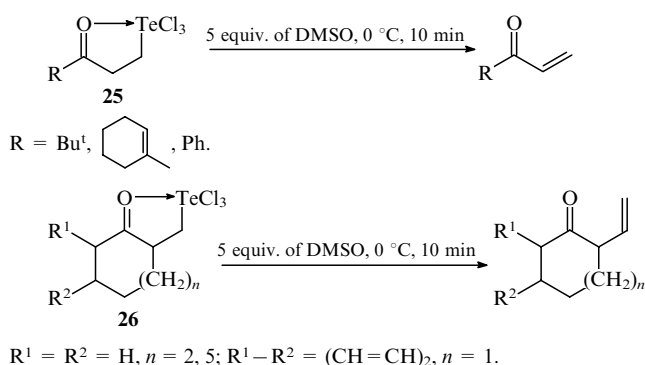


$\text{Ar} = 4\text{-MeOC}_6\text{H}_4, \text{1-naphthyl}, \text{2-naphthyl}$.

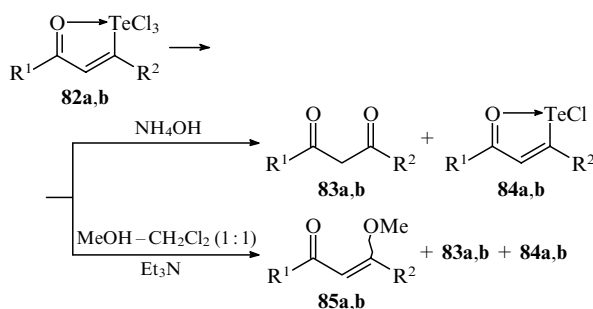
It is believed²⁰⁹ that carbonylation of aryltellurium trichlorides proceeded according to a scheme involving intermediate aryltelluriocarbonylnickel dichloride **81**.



In some cases, the direction of detelluration of organyltellurium trichlorides under the action of nucleophiles is governed by the presence of intramolecular $O \rightarrow TeCl_3$ coordinate bonds. Thus detelluration of β -trichlorotellurio ketones **25** and **26** proceeded smoothly under the action of basic agents, such as DMSO or amines.⁸⁵



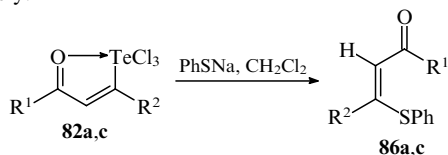
In the reactions with NH_4OH , σ -telluranes **82a,b** containing intramolecular $O \rightarrow Te$ coordinate bonds underwent detelluration with elimination of metallic tellurium to form a mixture of ketones **83a,b** (the yields were 56%–63%) and tellurenyl halides **84a,b** (the yields were 13%–36%).¹⁶⁹



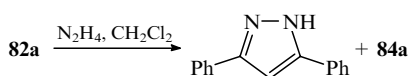
$R^1 = R^2 = Ph$ (a); $R^1 = Ph, R^2 = Me$ (b).

The reactions of the organyltellurium trichlorides **82a,b** with Et_3N in a 1:1 CH_2Cl_2 – $MeOH$ mixture afforded enol methyl ethers **85a,b** (a mixture of stereoisomers, the yields were 56%–80%). The ketones **83a,b** and the tellurenyl halides **84a,b** (in trace amounts) were isolated as by-products.¹⁶⁹

Detelluration of the ketones **82** proceeded under the action of other nucleophiles as well. Thus the reactions of the compounds **82a,c** with sodium benzenethiolate afforded exclusively *Z*-isomers of vinyl ketones **86a,c** in 74%–82% yields, whereas the reaction of the ketone **82a** with hydrazine gave rise to 3,5-diphenylpyrazole and the tellurenyl halide **84a** in 44% and 22% yields, respectively.¹⁶⁹



$R^1 = R^2 = Ph$ (a); $R^1 = 3-FC_6H_4, R^2 = Ph$ (c).



IV. Structures of σ -telluranes $RTeX_3$ in the crystalline state and in solution. Electronic effects of TeX_3 groups

1. Crystal structures of σ -telluranes $RTeX_3$

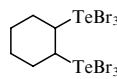
According to the polarity rule²¹⁰ extended to σ -telluranes,^{211,212} the axial positions in trigonal bipyramids in molecules of these compounds should be occupied by the most electronegative substituents. However, the real structures of a large number of σ -telluranes $RTeX_3$, being determined by the nature of both the electronegative substituents at the tellurium atom and the organic ligands, rarely correspond to trigonal bipyramids predicted theoretically. Three major groups of σ -telluranes $RTeX_3$, which differ in the degree of association in the crystalline state and in the coordinate bonding to the tellurium atom, can be distinguished. Organyltellurium trihalides $RTeHal_3$ whose organic ligands do not contain substituents capable of forming intramolecular coordinate bonds with tellurium atoms belong to the first group. The second group consists of organyltellurium trihalides containing an intramolecular $O(N) \rightarrow Te$ coordinate bond. The third group comprises σ -telluranes $RTeX_3$ containing bidentate (primarily, dithiocarbamate) ligands.

The data on the bond lengths, bond angles and types of associates in organyltellurium trihalides $RTeX_3$ whose organic ligands do not contain substituents capable of forming intramolecular coordinate bonds with tellurium atoms are given in Table 1.

Taking into account secondary interactions, the tellurium trihalides listed in Table 1 contain a pentacoordinate tellurium atom. The major structural unit in these compounds ($CTeX_4$) is characterised by a square-pyramidal configuration of the bonds about the tellurium atom, the organic radical being located in the apical position. The tellurium atom lies virtually in the base of the square pyramid formed by four halogen atoms (the deviation from the plane is insignificant). Two halogen atoms form shorter (terminal) bonds, whereas the two remaining halogen atoms are involved in longer (bridging) bonds through which the tellurium atoms are linked in polymeric or dimeric structures. The dimers are linked to each other through weak secondary bonds, which are substantially longer than the $Te-X_{bridge}$ bonds. σ -Telluranes containing two $TeHal_3$ groups bound to one carbon atom [for example, methylenebis(tellurium trichloride)²¹⁷] or to the vicinal carbon atoms [for example, 1,2-bis(tribromotellurio)cyclohexane²¹⁹] have monomeric structures. The bonds about each tellurium atom in these compounds adopt the square-pyramidal configuration, except that both bridging $Te-X$ bonds are intramolecular.

2-Biphenyltellurium trihalides containing the bulky 2-biphenyl radical also have monomeric structures with a trigonal-bipyramidal arrangement of the ligands about the tellurium atom.^{126,132,220} The axial positions are occupied by the halogen atoms. The angle between the axial bonds in 2-biphenyltellurium tribromide is 178.5°. The corresponding angles in the α and β modifications of the triiodide are 176.5° and 176.0°, respectively. The axial $Te-X$ bonds are substantially longer than the equatorial bonds in accordance with the polarity rule.²¹⁰ Short intramolecular $Te \cdots C$ contacts are observed in 2-biphenyltellurium trihalides [2.945 Å in the tribromide and 3.32 and 3.18 Å in the α and β modifications of the triiodide, respectively; the sum of the van der Waals radii of the tellurium and carbon atoms is 3.90 Å (see Ref. 221)]. Due to these contacts, 2-biphenyltellurium trihalides are readily converted into 5,5-dihalogenodibenzotellurophenes upon heating.⁸ Two modifications of 2-biphenyltellurium triiodide are structurally similar and differ only in intermolecular contacts involving the heavy atoms. In the β modification, the $I \cdots I$ contacts (3.337 Å) occur along with the secondary $Te \cdots I$ contacts,²²⁰ whereas two $I \cdots I$ contacts (3.239 and 3.772 Å) are observed in the α modification.¹³² The difference in the character of these intermolecular interactions is reflected in the colour of the compounds, viz., the crystals of the α and β

Table 1. Average bond lengths (Å) and bond angles (deg) in σ -telluranes $R\text{TeX}_3$.

Compound	Bond length				Bond angle		Type of the associate	Ref.
	Te–X _{term}	Te–X _{bridge}	Te···X	Te–C	C–Te–X _{term}	C–Te–X _{bridge}		
C ₂ F ₅ TeF ₃	1.872	2.913	—	2.20	88.8	77.6	polymer	138
ClCH ₂ CH ₂ TeCl ₃	2.386	2.717	—	2.164	92.7	82.5	"	98
PhTeCl ₃ (see ^a)	2.377	2.755	—	2.122	91.68	85.46	"	213, 214
4-EtOC ₆ H ₄ TeCl ₃	2.396	2.749	—	2.12	91.0	88.2	"	121
4-PhOC ₆ H ₄ TeCl ₃	2.374	2.768	3.702	2.111	91.3	87.2	dimer	216
CH ₂ (TeCl ₃) ₂	2.351	2.760	—	2.120	90.8	75.6	monomer	217
PhTeBr ₃	2.526	2.829	—	2.140	92.2	85.4	polymer	218
4-EtOC ₆ H ₄ TeBr ₃	2.531	2.932	4.143	2.10	93.6	88.4	dimer	121
2-PhC ₆ H ₄ TeBr ₃	2.490, ^b 2.661 ^c	—	3.713	2.136	—	—	monomer	126
	2.541	2.88	—	2.224	92.4	83.2	"	219
4-MeOC ₆ H ₄ TeI ₃	2.788	3.153	3.827	2.15	94.6	89.7	dimer	121
2-PhC ₆ H ₄ TeI ₃ - α	2.769, ^b 2.966 ^c	—	see ^d	2.15	—	—	monomer	132
2-PhC ₆ H ₄ TeI ₃ - β	2.748, ^b 2.928 ^c	—	see ^e	2.153	—	—	"	220

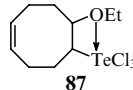
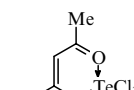
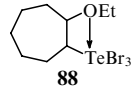
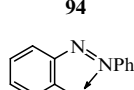
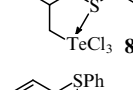
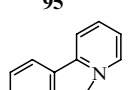
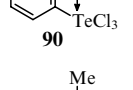
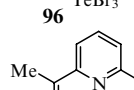
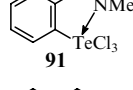
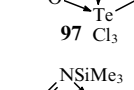
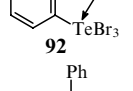
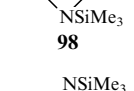
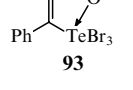
^a Phenyltellurium trihalide PhTeCl_{1.7}Br_{1.3} prepared by the reaction of equimolar amounts of TeCl₄ and Ph₂BBr also has a polymeric structure;²¹⁵ ^b the Te–X_{eq} bond length; ^c the average Te–X_{ax} bond length; ^d the lengths of the I···I secondary bonds are 3.239 and 3.772 Å; ^e the lengths of the Te···I and I···I secondary bond are 3.703 and 3.337 Å, respectively.

modifications of 2-biphenyltellurium triiodide are black and red, respectively.

The degree of association and, what is more important, the molecular geometry of organytellurium trihalides are changed substantially if the molecules contain substituents with donor

atoms (oxygen, nitrogen or sulfur) capable of being involved in intramolecular coordination with the tellurium atom. The results of X-ray diffraction studies of these compounds are given in Table 2.

Table 2. Average bond lengths (Å) and bond angles (deg) in σ -telluranes $R\text{TeX}_3$ containing intramolecular coordinate bonds.

Compound	Bond length			Bond angle		Ref.	Compound	Bond length			Bond angle		Ref.
	C–Te	Te–X	Y···Te ^a	CTeX	XTeX			C–Te	Te–X	Y···Te ^a	CTeX	XTeX	
	2.172	2.505, 2.481, 2.355	2.419	93.7	176.2	105		2.135	2.516, 2.486, 2.364	2.438	92.4	172.8	224
	2.29	2.665, 2.653, 2.502	2.49	95.1	172.9	222		2.114	2.491, 2.483, 2.406	2.417	92.9	171.7	57
	2.139	2.555, 2.453, 2.424	2.763	87.9	168.9	106		2.110	2.673, 2.658, 2.589	2.244	92.5	172.4	24
	2.108	2.324, 2.477, 2.497	2.972	90.02	174.9	223		2.129	2.500, 2.491, 2.438	2.402, ^b 2.878 ^c	88.4	171.3	83
	2.078	2.538, 2.465, 2.447	2.406	92.6	175.4	117		2.096, 2.192 ^d	2.489, 2.479, 2.434	—	—	172.1	32
	2.12	2.758, 2.633, 2.632	2.42	92.4	178.7	116		2.056, 2.185 ^d	2.550, 2.496, 2.488	—	—	177.1	225
	2.175	2.661, 2.659, 2.513	2.362	95.0	—	169							

^a Y = O, S or N; ^b the N → Te coordinate bond length; ^c the O → Te coordinate bond length; ^d the N–Te bond lengths are given; ^e in the complex with CH₂Cl₂.

8-Ethoxycyclooct-4-enyltellurium trichloride (**87**), like other organyltellurium trichlorides, adopts a square-pyramidal configuration. The carbon atom occupies the vertex of the pyramid. The base of the pyramid is formed by three chlorine atoms (the Cl—Te bond lengths have standard values; 2.335–2.505 Å) and the oxygen atom (in other σ -telluranes RTeCl_3 , four chlorine atoms lie in the base of the pyramid, two of these atoms being bridging). The Te $\cdots$ O distance (2.419 Å) is substantially smaller than the sum of the van der Waals radii of the tellurium and oxygen atoms (3.60 Å). In the crystals, there are also very weak secondary Te $\cdots$ Cl bonds (3.558 Å) through which the molecules are linked in dimers. Apparently, 2-ethoxycycloheptyltellurium tribromide (**88**),²²² 2-chloro-3-(allylthio)propyltellurium trichloride (**89**)¹⁰⁶ and 2-(phenylthio)phenyltellurium trichloride (**90**)²²³ have analogous structures.

In organyltellurium trihalides **91–96**, the bonds at the tellurium atoms adopt an octahedral configuration. Two halogen atoms are located in the apical positions. The equatorial positions are occupied by the third halogen atom, the bidentate organic ligand and the lone electron pair of the tellurium atom. Some compounds of this type have monomeric structures. In crystals of other compounds, the molecules are linked in dimers through intermolecular Te $\cdots$ X bonds. However, the lengths of these bonds (3.498 Å in the trichloride **91** and 3.596–3.896 Å in the tribromides **92**, **93** and **96**) are substantially larger than the lengths of the bridging Te—X bonds (see Table 1) and are close to the sums of the van der Waals radii of the corresponding elements. The N $\rightarrow$ TeX₃ coordinate bond lengths are in the range of 2.24–2.42 Å. The hybridisation state of the nitrogen atom affects only slightly the coordinate bond lengths.

The organic ligand in (6-acetyl-2-pyridyl)carbonylmethyltellurium trichloride (**97**) is polydentate, which results in a new structural type.⁸³ The coordination polyhedron about the tellurium atom can be described as a distorted pentagonal bipyramid with two axial Te—Cl bonds (2.492 and 2.500 Å). The equatorial positions are occupied by the Cl atom (Te—Cl_{eq} is 2.431 Å), three atoms of the tridentate organic radical, *viz.*, the carbon (Te—C is 2.129 Å), nitrogen (Te $\cdots$ N is 2.402 Å) and oxygen atoms (Te $\cdots$ O is 2.878 Å), and the lone electron pair of the tellurium atom. The two last-mentioned bond lengths, though larger than the sums of the covalent radii of the corresponding elements (the sum of the Te and N radii is 2.07 Å and the sum of the Te and O radii is 2.03 Å), are substantially smaller than the sums of the van der Waals radii of these elements (the sum of the Te and N 3.70 Å and the sum of the Te and O radii is 3.60 Å²²¹). The presence of the Te $\rightarrow$ N and Te $\rightarrow$ O coordinate bonds was also confirmed by IR spectroscopy.

Selected data for organyltellurium trichlorides containing N $\rightarrow$ TeCl₃ bonds (compounds **98** and **99**) are also given in

Table 2. The N $\rightarrow$ Te bond lengths in these compounds have close values (the differences are only 0.1–0.12 Å). The four-membered PN₂Te ring in the compound **99** is virtually planar. The nitrogen atoms deviate from the plane of the ring by ~ 0.05 Å.²²⁵

σ -Telluranes containing *N,N*-diorganylthiocarbamate ligands (**100a–g**) have analogous structures. Selected structural data for these compounds are listed in Table 3.

Compounds **100a–g** have pentagonal-bipyramidal structures. The equatorial positions of the bipyramid are occupied by five sulfur atoms (compounds **100a,b**) or four sulfur atoms and one halogen atom (compounds **100c–g**). In the tris(dithiocarbamate) derivative **100a**, the axial positions are occupied by the organic group and the sulfur atom of a dithiocarbamate ligand.^{226, 227} In the bis(dithiocarbamate)(dithiophosphate) derivative **100b**, the position of the second axial ligand is occupied by a sulfur atom of the S₂P(OEt)₂ group.¹⁴⁸ In the other compounds, the lone electron pair of the tellurium atom¹⁴⁸ or an atom of the adjacent molecule^{149–151} serves as the second axial ligand. The compounds **100a,b,d** exist as monomers, whereas molecules **100c,e–g**^{149–151} are linked as dimers through weak intermolecular Te $\cdots$ S or Te $\cdots$ Hal bonds.

The reason for the presence of secondary bonds of different nature in the compounds **100c,g** containing virtually identical substituents at the tellurium atom (one bromine atom in the compound **100c** or bromine and iodine atoms in a ratio of 41 : 59 in the compound **100g**) remains unclear. Thus the coordination polyhedron about the tellurium atom in the compound **100c** is completed by the weakly π -coordinated dithiocarbamate ligand of the adjacent molecule,¹⁵⁰ whereas the coordination polyhedron in the compound **100g** is completed by the bromine (iodine) atom.¹⁵¹

The structure of (4-methoxyphenyl)tellurium [(dimethoxythiophosphorylthio)] dibromide, (4-MeOC₆H₄)Te[S₂P(OMe)₂]₂.Br₂, differs from that of bis-(and tris)(dithiocarbamate) derivatives **100a–g** due to the presence of one bidentate ligand in the former compound. The molecule of this compound has a distorted square-pyramidal structure with the bromine atoms (Te—Br bond lengths are 2.616 and 2.677 Å) in *cis* positions relative to each other.¹⁵³ The sulfur atoms of the thiophosphorylthio ligand (the Te—S bond lengths are 2.632 and 2.728 Å) lie in the base of the pyramid. The aryl group (the Te—Br bond length is 2.127 Å) occupies the apical position. In the crystal, weak secondary Te $\cdots$ Br bonds (3.810 Å) are also present.

The structures of σ -telluranes RTeX_3 were also studied by NQR²²⁸ and Mössbauer spectroscopy.^{146, 229–232} The isomer chemical shifts for aryltellurium trichlorides, tribromides and triiodides in the region of 0.9–1.0 mm s^{−1} are substantially larger than those for the corresponding diaryltellurium dihalides and are

Table 3. Average bond lengths (Å) and bond angles (deg) in σ -telluranes containing *N,N*-diorganylthiocarbamate ligands $\text{R}^1\text{Te}(\text{S}_2\text{CNR}^2)_2\text{X}$ (**100a–g**).

Compound	R ¹	R ²	X ^a	Bond length				Bond angle C—Te—X	Ref.
				Te—C	Te—S	Te—X	secondary bonds		
a	Ph	Et	S ₂ CNEt ₂	2.124	2.606–2.816; ^b 3.228	—	—	144.6	226, 227
b	Ph	Et	S ₂ P(OEt) ₂	2.14	2.674–2.700 ^c	2.708, 3.436	—	148.0	148
c	4-MeOC ₆ H ₄	Me	Br ^d	2.145	2.623–2.717 ^c	2.890	3.751(Te $\cdots$ C)	107.20	150
d	Me	Et	I	2.115	2.618–2.723 ^c	3.117	—	—	148
e	Ph	Et	I	2.153	2.625–2.716 ^c	3.126 ^e	3.823, 3.598 (Te $\cdots$ S)	166.1, 154.8	149
f	4-MeOC ₆ H ₄	Et	I	2.211	2.626–2.733 ^c	3.169	3.569 (Te $\cdots$ I)	176.7	151
g	4-MeOC ₆ H ₄	Et	I _{0.59} Br _{0.41} (see ^f)	2.151	2.624–2.728 ^c	3.164, ^g 2.904 ^h	3.558 (Te $\cdots$ I), 3.476 (Te $\cdots$ Br)	174.9, 176.3	151

^a X is the ligand occupying the second axial position; ^b the range of the five Te—S bonds in the equatorial plane is given; ^c the range of the four Te—S bonds in the equatorial plane is given; ^d solvated with 0.5 equiv. of CH₂Cl₂; ^e the average Te—I bond length for two crystallographically independent molecules is given; ^f the compound was prepared by the reaction of bis(*N,N*-diethylthiocarbamate)(iodo)(4-methoxyphenyl)tellurium(IV) with bromine; ^g the Te—I bond length; ^h the Te—Br bond length.

similar to those for tellurium tetrahalides.²²⁹ The quadrupole splitting (5.9–9.3 mm s⁻¹) decreases in the order: chlorides > bromides > iodides.

2. Structures of organytellurium trihalides in solutions. ¹²⁵Te NMR spectra and dipole moments

The conductivities of solutions of organytellurium trichlorides RTeCl₃ in MeCN, PhNO₂ and Me₂CO^{73, 74, 194, 233} indicate that these compounds do not dissociate into ions. However, organytellurium tribromides and triiodides in these solvents dissociate into ions (RTeX₂⁺ and X⁻),^{73, 74} although Chen and George²³⁴ stated that MeTeBr₃ in nitrobenzene is not an electrolyte. On the contrary, aryltellurium trihalides containing amino(dimethylamino) groups in the aryl fragments are 1:1 electrolytes in the above-mentioned solvents regardless of the nature of the halogen atom.^{61, 62} Apparently, this is due to the higher polarity of the Te–Hal bonds in the latter compounds owing to the presence of strong electron-donor groups.

The results of cryoscopic studies of organytellurium trihalides agree on the whole with the data on conductivity. In solutions, aryltellurium trichlorides [except for amino(dimethylamino) derivatives] exist as monomers and tend to form weak associates as the concentration is increased,^{74, 194, 233} whereas aryltellurium tribromides and triiodides partially dissociate.^{61, 62, 73, 74} In the case of methyltellurium trihalides, the monomer–dimer equilibrium exists in benzene,^{118, 234} the degree of association of methyltellurium tribromide being higher than that of the corresponding trichloride.

The above-considered data agree with the results of spectral studies of organytellurium trihalides. The ¹²⁵Te NMR spectral data for σ-telluranes RTeX₃ are given in Table 4.

The chemical shifts of alkyltellurium and aryltellurium trihalides are in the ranges of 647–1204 and 892–1234 ppm, respectively. In the spectra of organytellurium trichlorides with ligands containing carbonyl groups, the ¹²⁵Te resonance is substantially shifted downfield (1372–1632 ppm) compared to the spectra of alkyltellurium trichlorides. The highest deshielding of the ¹²⁵Te nuclei is observed in β-arylvinylltellurium trichlorides whose chemical shifts are in the range of 2047–2104 ppm. The shielding of the ¹²⁵Te nuclei in PhTe increases on going from phenyltellurium trichloride to phenyltellurium triiodide. It should be noted that the chemical shifts of organytellurium trihalides depend substantially on the nature of the solvent. Thus the chemical shifts for PhTeCl₃ and PhTeBr₃ increase by 312 and 301 ppm, respectively, on going from the PhH–PhMe system to the 2:1 CH₂Cl₂–DMSO system. Apparently, this is associated with the above-mentioned effect of the solvent on the degree of aggregation of organytellurium trihalides in solution.

The dipole moments of aryltellurium trihalides are given in Table 5. The dipole moments of aryltellurium tribromides are smaller than those of the corresponding trichlorides regardless of the substituents in the benzene ring,²¹¹ which is indicative of a weaker electron-withdrawing effect of the TeBr₃ group compared to that of the TeCl₃ group.

Table 4. Chemical shifts in the ¹²⁵Te NMR spectra of σ-telluranes RTeX₃.

R	X	Solvent	δ ^a /ppm	Ref.	R	X	Solvent	δ ^a /ppm	Ref.
Me	Cl	PhH–PhMe	758	35	Ph	Br	CH ₂ Cl ₂ –DMSO (2:1)	1193	236
Me	Br	PhH–PhMe	647	35	Ph	I	CH ₂ Cl ₂ –DMSO (2:1)	1101	236
Cl ₃ TeCH ₂	Cl	DMSO	1198	235 ^b	4-BrC ₆ H ₄	Cl	CH ₂ Cl ₂ –DMSO (2:1)	1208	236
Et	Cl	PhH–PhMe	900	35	4-ClC ₆ H ₄	Cl	CH ₂ Cl ₂ –DMSO (2:1)	1208	236
Et	Br	PhH–PhMe	849	35	4-MeC ₆ H ₄	Cl	CH ₂ Cl ₂ –DMSO (2:1)	1234	236
Pr	Cl	PhH–PhMe	920	35	4-PhOC ₆ H ₄	Cl	CH ₂ Cl ₂ –DMSO (2:1)	1226	236
Pr	Br	PhH–PhMe	1204	35	4-MeOC ₆ H ₄	Cl	DMSO	1246	236
MeCOCH ₂	Cl	CHCl ₃	1372	79	4-MeOC ₆ H ₄	Br	CH ₂ Cl ₂ –DMSO (2:1)	1204	236
MeCOCHMe	Cl	CHCl ₃	1483	79	4-MeOC ₆ H ₄	I	CH ₂ Cl ₂ –DMSO (2:1)	1078	236
MeCOCHEt	Cl	CHCl ₃	1488	79	PhCOCH=CMe	Cl	CD ₂ Cl ₂	2053 ^c	237
MeCOCMe ₂	Cl	CHCl ₃	1632	79	PhCOCH=CMe	Br	CD ₂ Cl ₂	2074 ^c	237
EtCOCH ₂	Cl	CHCl ₃	1374	79	PhCOCH=CPh	Cl	CD ₂ Cl ₂	2047 ^c	237
EtCOCHMe	Cl	CHCl ₃	1485	79	4-MeC ₆ H ₄ COCH=CPh	Br	CD ₂ Cl ₂	2086 ^b	237
EtCOCHEt	Cl	CHCl ₃	1488	79	1-C ₁₀ H ₇ COCH=CPh	Cl	CD ₂ Cl ₂	2053 ^c	237
EtCOCMe ₂	Cl	CHCl ₃	1621	79	1-C ₁₀ H ₇ COCH=CPh	Br	CD ₂ Cl ₂	2104 ^c	237
PrCOCH ₂	Cl	CHCl ₃	1376	79	2-PhN=NC ₆ H ₄	Cl	CDCl ₃	1278	146
PrCOCHMe	Cl	CHCl ₃	1484	79	Ph	S ₂ CNEt ₂	THF	1455	148
PrCOCHEt	Cl	CHCl ₃	1490	79	Ph	S ₂ CNEt ₂	CH ₂ Cl ₂	1472	148
PrCOCMe ₂	Cl	CHCl ₃	1625	79	Me	S ₂ CNEt ₂	CH ₂ Cl ₂	1673	148
Pr ⁱ COCH ₂	Cl	CHCl ₃	1373	79	2-PhN=NC ₆ H ₄	S ₂ CNMe ₂	CDCl ₃	1225	146
Pr ⁱ COCHMe	Cl	CHCl ₃	1482	79	2-PhN=NC ₆ H ₄	S ₂ CN(CH ₂ Ph) ₂	CDCl ₃	1240	146
Bu ⁱ COCH ₂	Cl	CHCl ₃	1373	79	Ph	(S ₂ CNEt ₂) ₂ Cl	THF	1622	148
Bu ⁱ COCHMe	Cl	CHCl ₃	1489	79	Ph	(S ₂ CNEt ₂) ₂ Cl	THF ^c	1660	148
Bu ⁱ COCH ₂	Cl	CHCl ₃	1364	79	Me	(S ₂ CNEt ₂) ₂ I	CH ₂ Cl ₂	1892	148
Bu ⁱ COCHMe	Cl	CHCl ₃	1487	79	Ph	(S ₂ CNEt ₂) ₂ Cl ₂	THF ^{d, f}	1098	148
Ph	Cl	PhH–PhMe	917	35	Ph	(S ₂ CNEt ₂) ₂ Y	CH ₂ Cl ₂	1563	148
Ph	Cl	THF ^c	532	148	Ph	(S ₂ CNEt ₂) ₂ Y	CH ₂ Cl ₂ (see ^d)	1612	148
Ph	Cl	DMF ^d	524	148	Me	(S ₂ CNEt ₂) ₂ Y	CH ₂ Cl ₂ (see ^f)	1768	148
Ph	Cl	DMSO	503	148	Me	(S ₂ CNEt ₂) ₂ Y	CH ₂ Cl ₂ (see ^{c, f})	1796	148
Ph	Cl	CH ₂ Cl ₂ –DMSO (2:1)	1229	236	Ph	(S ₂ CNEt ₂) ₂ Z	CH ₂ Cl ₂ (see ^f)	1510	148
Ph	Br	PhH–PhMe	892	35	Me	(S ₂ CNEt ₂) ₂ Z	CH ₂ Cl ₂ (see ^f)	1722	148

Note: Y = S₂P(OEt)₂; Z = S₂COEt; ^a the chemical shifts are given relative to Me₂Te; ^b for (Cl₃TeCH₂CO)₂O, δ_{125Te} = 864 ppm;²³⁵ ^c at –80 °C; ^d at –40 °C; ^e Ph₂Te was used as the standard (δ_{Me₂Te} = δ_{Ph₂Te} + 688); ^f the spectrum of a solution prepared by mixing of the corresponding substrates.

Table 5. Dipole moments of aryltellurium trihalides $\text{RC}_6\text{H}_4\text{TeX}_3$ (dioxane, 25 °C).²¹¹

R	X	μ_{exp}	μ_{calc}	R	X	μ_{exp}	μ_{calc}
H	Cl	3.66 ^a	—	4-MeO	Br	3.88	3.79
H	Br	3.35	—	4-NO ₂	Cl	4.13	4.14
4-Me	Cl	3.94	3.84	3-NO ₂	Cl	5.16	4.95
4-Me	Br	3.51	3.57	3-F	Cl	3.76	3.89
4-Cl	Cl	3.33	—	4-OH	Cl	4.20	3.97
4-Cl	Br	2.62	2.78	4-MeS	Cl	4.23	4.02
4-Br	Cl	3.20	3.32	3,4-(MeO) ₂	Cl	4.36	4.33
4-Br	Br	2.78	—	3,4-Me ₂	Cl	4.01	4.0
4-MeO	Cl	4.61	4.04				

^a The dipole moment of PhTeCl_3 in C_6H_6 (40 °C) is 2.90 D.²³⁸

3. Electronic effects of the TeX_3 groups

The inductive and mesomeric constants of the TeX_3 groups were determined based on the chemical shifts in the ^{19}F NMR spectra of *m*- and *p*-fluorophenyltellurium trihalides.¹¹⁴

Substituent	$\delta_{\text{meta}}^{\text{F}}/\text{ppm}$	$\delta_{\text{para}}^{\text{F}}/\text{ppm}$	σ_{I}	σ_{C}	σ_{P}
TeCl_3	−3.28	−6.62	0.55	0.11	0.66
TeBr_3	−3.05	−6.43	0.51	0.11	0.62

The σ_{I} and σ_{C} values indicate that interactions between the TeX_3 groups and the π -electron system of the benzene ring are predominantly inductive in character because the σ_{C} constants comprise ~15% of the total electronic effect of the substituent. The σ_{P} constants of the TeX_3 groups, unlike those of the $\text{Te}(\text{R})\text{X}_2$ groups ($\text{X} = \text{F}, \text{Cl}, \text{Br}$ or I), decrease on going from chlorine to bromine.

The orbital populations were calculated and the nature of the highest bonding and lowest unoccupied orbitals of PhTeCl_3 was examined using the extended Hückel method.²¹¹ According to the results of calculations, the π -electron system of the benzene ring is only slightly affected by the substituent and retains six electrons. A large positive charge on the tellurium atom exists due to the fact that its *p* orbitals and the combination of the *p_x* and *p_z* orbitals of the axial chlorine atoms with the appropriate symmetry are combined into the molecular orbital $\text{MO}_{\pi}(\text{E}_{1\text{a}})$.

Calculations demonstrated that the three highest occupied MOs are σ orbitals. The upper orbital is localised primarily at the tellurium atom, whereas the unoccupied orbital, which involves the d_{π} orbital of the tellurium atom, (MO_{34}) is far removed from the highest occupied π -MOs. These quantum-chemical data account for the absence of a noticeable effect of conjugation between the TeCl_3 group and the aryl groups.

V. Conclusion

The data surveyed in the present review suggest that σ -telluranes RTeX_3 are of preparative importance in the chemistry of organotellurium compounds. σ -Telluranes are used as the starting compounds in the synthesis of other classes of organic derivatives of tellurium, *viz.*, of diorganyl ditellurides R_2Te_2 , tellurinic acids $\text{RTe}(\text{O})\text{OH}$, tellurium oxochlorides $\text{RTe}(\text{O})\text{Cl}$, σ -telluranes of the R_2TeX_2 type and pentacoordinate tellurium derivatives $\text{M}^+[\text{RTeX}_4]^-$ (M is the onium group). Intramolecular electrophilic cyclisation of the corresponding organytellurium trichlorides is used for the preparation of different five- and six-membered tellurium-containing heterocycles (benzotelluophenes, dibenzotelluophenes and telluroxanthenes) and six-membered heterocycles involving other heteroatoms along with the tellurium atom (phenoxatellurines, phenothiatellurines and phenotellurazines). These reactions are specific to the synthesis of tellurium-containing heterocycles and have virtually no analogues in the chemistry of the corresponding sulfur and selenium derivatives. Halodetel-

luration of organytellurium trihalides, which in some cases proceeds with rather high yields, can be used for the preparation of biaryls, different types of mono- and dihalogeno derivatives, stilbenes, carboxylic acids and unsaturated ketones.

The development of new procedures for the synthesis of organytellurium trihalides, the synthesis of new tellurium-containing heterocycles starting from these compounds and examination of the possibilities of the use of these compounds in preparative organic chemistry are of obvious interest both in organotellurium chemistry and in organic chemistry as a whole.

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Polymer monolayers and Langmuir–Blodgett films. Polythiophenes

V V Arslanov

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Abstract. The structures and properties of monolayers and Langmuir–Blodgett films of conducting oligo- and polythiophenes are analysed. The published data on the influence of the number, size, and composition of substituents in polythiophene molecules and of the pattern of their distribution along the chain on the monolayer stability and Langmuir–Blodgett film quality are generalised. Considerable attention is given to the description of the behaviour of mixed monolayers and Langmuir–Blodgett films composed of polythiophenes and various amphiphilic compounds. The effective conjugation lengths of polymer chains and conductivities of polythiophenes in Langmuir–Blodgett films and cast films are compared. Examples of the use of Langmuir–Blodgett films for scientific and technological purposes are given. The bibliography includes 100 references.

I. Introduction

The Langmuir–Blodgett method is a versatile technique for assembling multilayer planar ensembles. The scope of problems that can be solved with the use of this method has expanded considerably over recent years. Polymer monolayers and Langmuir–Blodgett (LB) films play an important role in fundamental and applied molecular architecture studies. In the author's review,¹ the two-dimensional polymerisation of, mostly, traditional monomers and their analogues with hydrocarbon substituents incorporated in order to increase their amphiphilic properties was discussed. In the majority of cases, polymerisation in monolayers and LB films has been carried out by photo-irradiation of unsaturated compounds such as acrylate and methacrylate lipids, alkyl fumarates and maleates, unsaturated fatty acids, *etc.* Within the latter group of systems, diacetylenes and polydiacetylenic amphiphilic compounds belonging to conducting polymers were considered.

In another paper,² the structure and properties of polymer monolayers and LB films have been analysed. This paper dealt with the characteristic features of the packing of macromolecule

on the surfaces of liquids and solids, the compatibility of high- and low-molecular compounds in monolayers, the influence of the degree of polymerisation, size and orientation of side groups on the phase states of monolayers, the correspondence between the architectures of Langmuir and LB monolayers, and many other issues. However, this paper did not touch upon the so-called special polymers which include conducting macromolecules with conjugated bonds, polymers synthesised for nonlinear optics, and highly stable multifunctional network polymers. The abundance of recent data on the properties of monolayers and LB films of only conducting polymers does not allow a detailed analysis of these systems to be made in the framework of one publication. Therefore, the author intends to present separate discussions on the most promising conducting polymers in the form of LB films that are studied most extensively.

Polythiophenes occupy a particular place among these polymers (polydiacetylenes, polyaniline, polypyrrole, polyphenylenes, *etc.*), primarily because they are soluble in ordinary solvents, form rather stable monolayers on the surface of water in air and have relatively high stability and conductivity in a doped state.

Extensive studies of polymers with internal conductivity started back in the 1970s when polydiacetylene was synthesised.^{3,4} Conducting organic polymers have a quasi one-dimensional structure which, to some extent, is similar to that of charge-transfer complexes (CTC). In the conducting state, both types of materials exist as charged molecules. The conductivity of CTC is much higher along the axial direction of stacked molecules due to overlapping of the π -orbitals of the adjacent complexes. In the case of conducting polymers, charge transfer occurs along the chain due to overlapping of the π -orbitals of the adjacent monomeric units. Due to the chain-like structures of the conducting polymers, strong interactions of the electronic states with the excited conformation states (solitons, polarons, bipolarons) exist, which is typical of one-dimensional systems. The relatively weak interchain interactions provide the diffusion of dopant molecules to the polymeric chain. A decrease in the intensity of interchain interactions in polythiophenes containing substituents at positions 3 and 4 favours the solubility of the polymers in ordinary solvents. This is the most important feature of polythiophenes when deciding whether the Langmuir–Blodgett technique should be used for their organisation. For example, it was noted⁴ that the conductivity of non-substituted polythiophenes ranges from 50 to 100 S cm⁻¹, while it is as high as 500 S cm⁻¹ in the case of poly(3-methylthiophene) and is close to 1000 S cm⁻¹ for some substituted polythiophenes.

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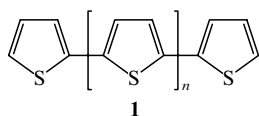
Polythiophenes are synthesised by chemical or electrochemical methods. The former method gives non-conducting polymers which can be transformed to the conducting state by chemical or electrochemical doping. In the latter case, doped (oxidised) polymers formed can be reduced chemically (de-doped) to the insulating state. The doping efficiency is determined from the position and intensity of the characteristic $\pi-\pi^*$ transition absorption band and from the change in the polymer colour. In addition, optical absorption spectra enable determination of the effective conjugation length of the polymeric chains. The longer the conjugation length the higher the polymer conductivity. The conjugation length can be increased by chemical synthesis of polythiophenes with a regular structure. As a result, the electric conductivity can be increased by a factor of 100 (Ref. 3).

The features of polythiophenes noted above are used for obtaining monolayers and LB films that are promising as metal and gas sensors, photoelectric and electrochromic devices, optical switches, solar batteries, *etc.*

The Langmuir–Blodgett method is used for the formation of planar ensembles of conjugated polymers in order to obtain ordered, similarly organised molecular chains, *i.e.*, to reach the longest possible conjugation length so as to increase the intramolecular conductivity and provide the transfer of charge carriers between the adjacent molecules. However, the potential of this method can only be realised if true monolayer films with concerted molecular orientation are formed on the surface of a liquid and if these monolayers can be transferred onto solid supports with the formation of multilayered ensembles. The success of these operations is usually judged from the structural or optical spectroscopy studies. The latter method makes it possible to estimate the zone structure features and evaluate the conjugation length of the system formed. Measurement of the conductivity of the LB films obtained is the final step. Depending on the ultimate goal of the studies, other properties of the systems, such as nonlinear optical, photo- and electrophysical properties, can also be determined. The majority of studies on the subject of this review have been carried out according to this scheme, hence it is reasonable to follow it when discussing their results.

It might seem that one glance at the polythiophene chain (**1**)[†] would suffice to make sure that these polymers cannot form stable monolayers on the surface of water and, even more so, on solid supports.

However, as shown below, not all researchers agree with this viewpoint.



The problem of increasing the stability of monolayers of compound **1** can be solved at least by two methods: *viz.*, by incorporation of groups that can enhance the surface activity of the molecule and by creation of mixed monolayers with amphiphilic compounds that form stable monolayers. The merits and drawbacks of these two methods for obtaining stable monolayers from molecules that are not 'strictly amphiphilic' are considered elsewhere.² It should be emphasised here that for polymers with distinct functions which depend, first, on the presence of certain reactive groups or conjugated bonds, and second, on realisation of a given conformation or structure of side chains determining the operating capabilities of molecules and their ensembles, incorporation of a second component is undesirable because it decreases the density of the key elements (functional groups, molecules, domains) in the layer and, as a consequence, decreases the efficiency of devices based on these elements. Therefore, the efforts of researchers are primarily aimed at synthesising such derivatives of polythiophenes whose spreading does not require

dilution with other components, *i.e.* at designing mixed monolayers with the matrix components possessing high surface activities. Let us note the main directions of these studies.

1. Grafting of a polar group to an end of the oligothiophene chain which in this case plays the role of the hydrophobic component of the amphiphilic molecule.

2. Incorporation of a side alkyl chain in each thiophene unit. This method works successfully in the case of linear polymers.²

3. Incorporation of one or two hydroxyalkyl groups, which increase the polarity of the thiophene components, in each thiophene unit.

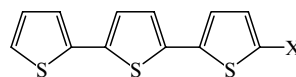
4. Copolymerisation (including block copolymerisation) of thiophene with other monomers that ensure distribution of the thiophene fragments over the subphase surface. In this case it is important that the second component also had conjugated bonds.

5. Synthesis of regioregular poly(3-R-thiophenes), where R is an alkyl, alkoxy or some other group.

However, these methods do not guarantee the desired result; therefore, mixed systems are studied, in which the functional capabilities of the key elements are preserved, provided that the component ratio remains at the optimum level.

II. Oligothiophene monolayers and Langmuir–Blodgett films

The effect of a polar group on the compression isotherms of a monolayer is shown in Fig. 1 for three-membered oligothiophenes **2–7** on the surface of water at 10 °C. One can see that compounds **2** and **3** do not form stable monolayers.² The esters **4–6** form condensed monolayers, in which the limiting area per molecule (A_0) is 27–29 Å². It is believed that this area corresponds to the vertical arrangement of terthiophene units that are directed towards the air phase, since they are more hydrophobic than the polar components of the oligomer molecules. Taking the parameters of the characteristic points in the compression isotherms of compounds **4–6** into account, Nakahara *et al.*⁵ concluded that the monolayers of these oligomers are stable up to surface pressures (π) of 20 (**4** and **5**) and 30 mN m⁻¹ (**6**).



2–7

X = CHO (**2**), CH₂OH (**3**), CH₂OCOMe (**4**), CH₂OCOCH=CMc₂ (**5**), CH₂OCO(CH₂)₇Me (**6**), CH₂OCO(CH₂)₁₆Me (**7**).

For the long-chain derivative **7**, the surface pressure for destruction is as small as several units, while the value of area per molecule extrapolated to zero surface pressure is no higher than 23 Å². In this case, a condensed monolayer is formed in

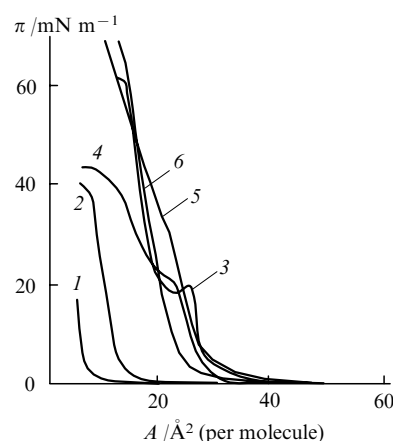


Figure 1. Compression isotherms of terthiophene derivatives at 10 °C:⁵ (**1**) **2**, (**2**) **3**, (**3**) **4**, (**4**) **5**, (**5**) **6**, (**6**) **7**.

[†] Henceforth, poly(2,5-diylthiophene) is considered in this review.

which dense packing of hydrocarbon chains probably exists, whereas the less hydrophobic terthiophene group can be immersed in the aqueous phase. The U-shaped configuration of molecules in the monolayer can be ruled out because the areas of the molecules are very small. Presumably, the capability of these compounds to give stable monolayers is overestimated: the isotherms of compound **4** are shifted to smaller areas with increase in temperature. Moreover, the possibility of ‘immersion into water’ of the thiophene groups is determined by interactions of their hydrocarbon substituents with water molecules rather than by the lengths of these substituents. Unfortunately, the data on the changes in the surface pressure following stopping of the mobile barrier of surface balances were not reported.

Monolayers of oligothiophenes with a larger number of units could be obtained only by mixing them with eicosanoic (arachidic) acid.⁵

Monolayers and LB films were obtained from the six-membered oligothiophene **1** ($n = 4$, S_6) using a strategy for the formation of one-dimensional conducting systems.⁶ The monolayers were transferred onto a solid support with the surface pressure of 15 mN m^{-1} and surface area per molecule (A) of $25 \text{ \AA}^2$. The chain orientation found from the dichroic ratio was vertical relative to the support (Fig. 2). The eighteen-layered LB films were thermally polymerised (270°C , 2.5 h). Comparison of the electronic spectra of LB films of the original oligomer S_6 and its thermal polymerisation product showed that the conjugation length in the latter was larger. It was also noted that the S_6 oligomer is completely soluble in nitrobenzene and trichlorobenzene, while the polymer synthesised in LB films is insoluble in these solvents.

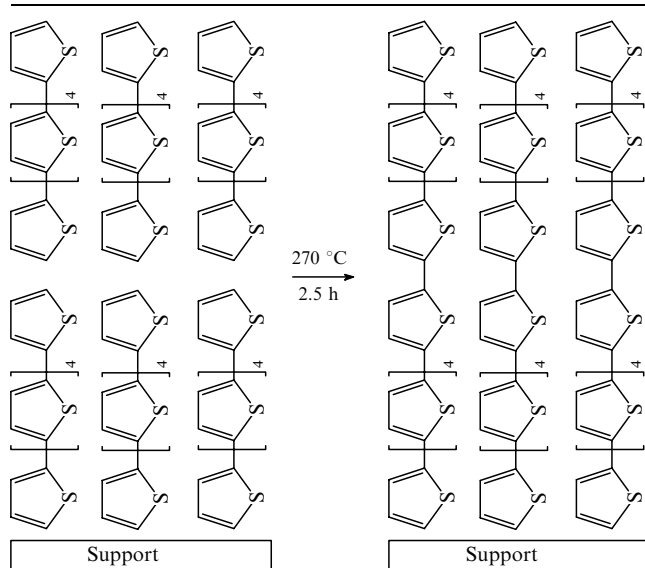
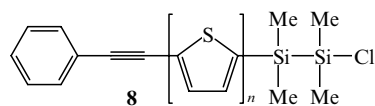
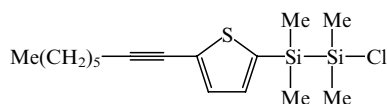


Figure 2. Organisation of six-membered thiophenes **1** (S_6) in LB films before and after thermal polymerisation.⁶

The solubility of oligothiophenes in various solvents and the possibility of coordination of their sulfur atoms with metals⁷ are the properties that attract the most attention in relation to the studies in the field of self-assembled monolayers,^{8–10} *i.e.*, systems very similar to LB films. A study of this kind was carried out for systems containing (oligo)thiophene unit(s) with 2-chlorotetramethyldisilanyl and phenylethynyl (compound **8**) or oct-1-ynyl substituents.^{11, 12}

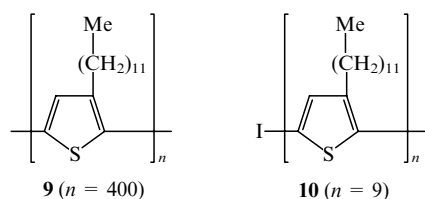


$n = 1, 2, 4$

The adsorption of the oligothiophene **8** from its solution in toluene was carried out onto a SiO_2 surface ($3000 \text{ \AA}$)/Si. The authors succeeded in obtaining self-assembled monolayers the density of which depended on the number of thiophene rings in the molecule and increased with the increase in the length of the oligomeric chain. Obviously, lateral conductivity requires a high density of the surface layer and at least six or seven thiophene units in the oligomer molecule are required for obtaining high transverse conductivity.^{13–17}

III. Polythiophene monolayers and Langmuir–Blodgett films

One attempt at obtaining monolayers and LB films from individual polythiophene derivatives has been undertaken by Logsdon *et al.*¹⁸ Poly(3-dodecylthiophene) was synthesised by electrochemical and chemical polymerisation. Electrochemical polymerisation of 3-dodecylthiophene was carried out under galvanostatic conditions at an anodic current density of 2 mA cm^{-2} at 5°C in an argon atmosphere using nitrobenzene as the solvent.¹⁹ The average molecular mass of the chloroform-soluble fraction of the polymer **9** is 10^5 Da . The chemical synthesis included three steps, *viz.*, synthesis of 3-dodecylthiophene,²⁰ its conversion to diiodo-3-dodecylthiophene²¹ and polymerisation.²² The molecular mass of the final product (**10**) determined by gel-permeation chromatography was $2.3 \times 10^3 \text{ Da}$.



The limiting areas per monomeric unit were 14.4 and $11.2 \text{ \AA}^2$, respectively, for monolayers of poly(3-dodecylthiophenes) synthesised chemically and electrochemically. The authors believe that, since the first value correlates with that of $14.7 \text{ \AA}^2$ calculated using the structural model for thiophene rings arranged at a right angle to the substrate surface, this particular orientation exists in the polythiophene monolayers synthesised chemically. If this is the case, the role of the hydrocarbon chain, the cross-section of which is $\sim 18.5 \text{ \AA}^2$, remains unclear. We shall return to this problem in the analysis of the structure of monolayers of other thiophene derivatives. It should be noted here that both specimens of poly(3-dodecylthiophene) spread poorly and do not form stable true monolayers on the surface of water.² The limiting area of the polythiophene monolayer synthesised chemically was larger than that of the thiophene monolayer obtained electrochemically, but the former monolayers were less stable and could not be transferred onto solid supports. The Langmuir–Blodgett vertical method ‘did not work’ in the case of the electrochemically polymerised poly(3-dodecylthiophene), either. However, the horizontal method at a surface pressure of 12 mN m^{-1} made it possible to transfer the monolayers and to obtain X-type films several tens layers thick on a solid support hydrophobised with trichlorooctadecylsilane. Unfortunately, diffraction methods were not used for structural studies of the resulting films, therefore the structure quality of these films cannot be judged.

Obviously, the films considered above may be, with caution, classified as LB films with distinct molecular orientation in the layers and alternation of the layers. This should be taken into account when considering the results of analysis of poly(3-do-

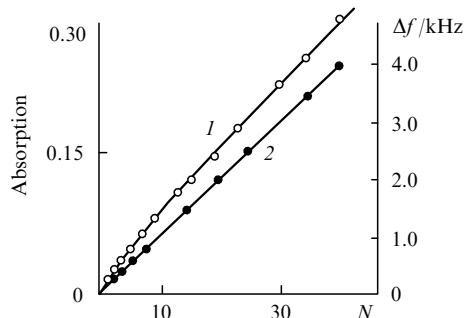


Figure 3. Dependence of optical absorption (1) and change in resonance frequency (f) of a quartz crystal (2) on the number of monolayers (N) of polythiophene **9**.¹⁸

decylthiophene) LB films presented below. Figure 3 shows the dependences of the optical absorption and the change in the quartz resonator frequency on the number of layers of the chemically polymerised poly(3-dodecylthiophene). The small inflexion on the plot of absorption *versus* the number of layers at $N = 10$ can be explained either by incomplete transfer of thick films onto the support due to the non-uniformity of the morphology of the surface formed or by a decrease in the structural correlation due to disordering of the polymeric segments. The monolayer thickness in LB film calculated from optical absorption data was found to be 35 Å. This value is closer to the result of ellipsometric thickness measurement (30 Å) than to the monolayer thickness determined using the structural model (19–24 Å). The linear dependence of the quartz resonator frequency on N indicates that the mass of the monolayer transferred onto the solid support is constant (the mass of one layer per 1 cm² is 350 ng) and that changes in the slope of the optical absorption on N are due to the orientation effects rather than to changes in the mass of the monolayers transferred. The specific electric conductivity of the non-doped film does not depend on the number of layers for $N \leq 40$ and equals 9×10^{-10} S cm⁻¹. Doping with iodine increases the conductivity by 8 orders of magnitude, and its minimum value depends on the number of layers: the conductivity for $N = 1, 20$ and 40 equals 0.014, 0.20 and 0.51 S cm⁻¹, respectively. The curves of changes in $\sigma_{||}$ (lateral conductivity) and absorption at 760 nm during the doping in iodine vapour are presented in Fig. 4. During the first 460 s, $\sigma_{||}$ increases by 6 orders and then reaches saturation in 4300 s. Flushing the cell with argon, which removes iodine from the system, restores the initial value of conductivity. The cubic susceptibility [$\chi^{(3)}$] of the non-doped film is as high as 1×10^{-9} electrostatic units. After doping, $\chi^{(3)}$ becomes 10% less and acquires its original value upon removal of iodine from the system.²³

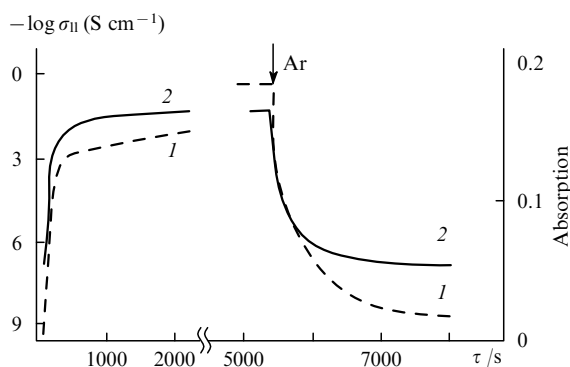


Figure 4. Dependences of the specific electric conductivity (1) and optical absorption (2) of a 40-layer LB film of polythiophene **9** on the time of exposure in iodine vapour and changes in these parameters after removal of iodine with a flow of argon.¹⁸

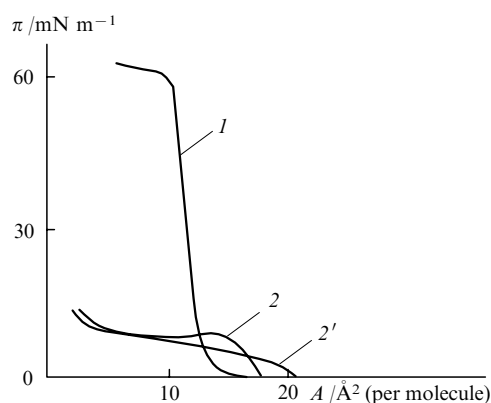
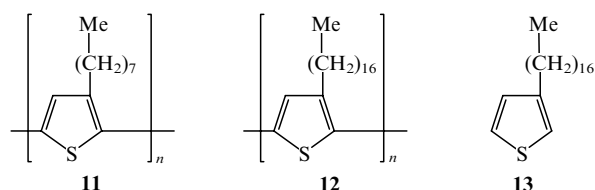


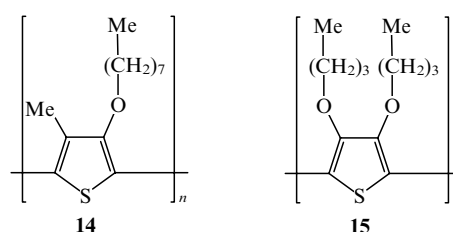
Figure 5. Compression isotherms of monolayers of polythiophene **12** (1) and its monomer **13** on the surface of water (2) and a 10^{-3} M CdCl₂ solution (2').²⁵

It should be emphasised that complex studies of poly(3-dodecylthiophene) LB films did not reveal any specific features of multilayer structures which would be untypical of this conjugated polymer in the bulk.

A decrease²⁴ or increase²⁵ in the length of the alkyl chain at position 3 of the thiophene ring in the polymer (from C₁₂ to C₈ or to C₁₇) virtually does not affect the ability of the polymer to form stable monolayers. The limiting area per unit for poly(3-octylthiophene) (**11**) monolayer does not exceed 10 Å², while that for poly(3-heptadecylthiophene) (**12**) does not exceed 12 Å² (Fig. 5). The small value of the limiting monolayer area obtained in the latter case is explained²⁵ by detachment of some fraction of molecules or their units from the surface of the aqueous subphase (incomplete spreading). According to ellipsometry, the layer thickness is 50% larger than that calculated for the monolayer, hence the small value of A_0 can also be due to the formation of a tilted bilayer structure.²⁵ Figure 5 also shows the compression isotherms for the 3-heptadecylthiophene monomer (**13**). One can see that transition to the monomer, which decreases the intrachain cohesion due to cleavage of the polymer covalent bonds, improves insignificantly the spreading of thiophene and results in a liquid monolayer with low decomposition pressure.



Thus, incorporation of an alkyl chain in the thiophene unit enhances insignificantly the spreading ability of the polymer due to weakening of the cohesion interactions between the thiophene rings. However, the hydrophilicity of the thiophene units remains rather low and does not ensure the formation of a stable monolayer on the surface of water. Incorporation of substituents at positions 3 and 4 of the thiophene ring, for example, of an alkoxy group to give poly(3-octyloxy-4-methylthiophene) (**14**), does not allow a true monolayer to be obtained on the surface of water.^{26, 27}



The idea of hydrophilisation of each thiophene ring in polythiophene was implemented by Callender *et al.*,²⁸ who have synthesised and studied the properties of monolayers of poly(3,4-dibutoxythiophene) (**15**). Polythiophene **15** was synthesised from 3,4-dibromothiophene and sodium butoxide in the presence of copper oxide and platinum iodide with subsequent chemical oxidation of the monomer with iron trichloride.

The compression isotherms of compound **15** at two temperatures are presented in Fig. 6. The monolayer destruction at 11 °C occurs above a surface pressure of 20 mN m⁻¹, which is believed to be due to folding of the monolayer and formation of a bilayer film. Destruction at higher temperatures is observed at lower π . The Langmuir–Blodgett films of polythiophene **15** were obtained at 11 °C and a surface pressure of 12 mN m⁻¹. Under these conditions, changes in π and A were negligibly small within 2 h and the limiting area per residue was 20 Å². It was found²⁹ that the surface of the thiophene chains, whose long axes are arranged at a right angle to the subphase surface and have a dihedral angle of 90°, is 28 Å². However, it was shown¹⁸ that a poly(thiophene) molecule, whose chains are parallel to the surface of water and the rings are oriented perpendicularly to this surface, requires a surface of 14.7 Å² per residue. In this case, the area per residue equal to 20 Å² found for polythiophene **15** should correspond to a polymer with an axis directed parallel to the surface of water and a dihedral angle between repeating units ranging from 0° to 90°. The resulting twisted conformation is formed due to steric interactions between the bulky alkoxy substituents at positions 3 and 4. The absorption spectrum of the 28-layer LB film of polythiophene **15** does not differ from the spectrum of this polymer in the solid state; the absorption intensity in the maximum (the band at 462 nm) increases linearly with an increase in the number of layers ($N \leq 30$). Optical spectroscopy was used to analyse the stability of polythiophene **15** LB films stored under various conditions:²⁸ in the dark, under daylight and under artificial light with a wavelength of > 500 nm. After ageing for 30 days, absorption at 462 nm did not change for the first sample, but it decreased by 35% and 24% for the second and third samples, respectively. The absorption maximum of polythiophene **15** LB films is shifted towards shorter wavelengths relative to the absorption maxima of solid poly(3-alkylthiophenes) (~ 500 nm)³⁰ and poly(3-butoxy-4-methylthiophene) (545 nm).²⁶ These data suggest that steric interactions between the two bulky side chains and the polymer chain favour the formation of such a polymer conformation where the thiophene units are turned relative to each other. This decreases the effective conjugation length. X-Ray diffraction data²⁸ indicate that the bulk polymer **15** is semicrystalline and has a helical conformation, which is apparently preserved in solution (chloroform). Since the polymer chain conformation and the LB film structure determine the electric²⁷ and nonlinear-optical properties to a considerable extent, structural studies of these systems have to be carried out.

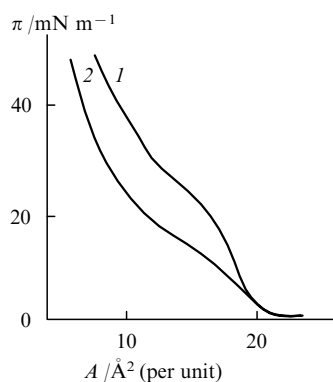


Figure 6. Compression isotherms of monolayers of polythiophene **15** on the surface of water at 11 (1) and 26 °C (2).²⁸

After their failure to obtain stable monolayers and LB films of poly(3-alkylthiophenes), Bolognesi *et al.*³¹ synthesised polythiophenes **16–18** containing ether groups at position 3.

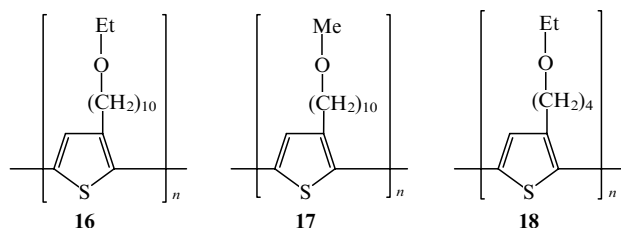


Figure 7 shows the compression isotherms of monolayers of polythiophenes **16–18**. One can see that the curves differ noticeably; the regions of area per residue exceeding 14.7 Å² (the minimum area occupied by the thiophene monomer) are the most interesting. The limiting areas per residue are 20, 15.5 and 15.3 Å² for the polymers **16–18**, respectively. Presumably, in all three cases the oxygen atoms in the monolayers are in contact with the aqueous support, whereas the differences in the areas are explained by different slopes of the hydrocarbon spacers in the side chains. The angle between the adjacent monomeric units should also be taken into account; the area per residue can vary from 28 to 14.7 Å² as a function of this angle. The pressures for monolayer collapse differ considerably as well: these are 20.0, 41.0 and 21.5 mN m⁻¹ for compounds **16**, **17** and **18**, respectively. The big difference between the collapse surface pressures (π_c) for polythiophenes **16** and **17**, whose side chains differ only in one CH₂ group, is unexpected. This fact was explained³¹ by the higher polarity of OMe-substituted polythiophene. However, this would imply that the more polar polymer **18** would form a more stable monolayer. In reality, the opposite phenomenon is observed (see Fig. 7). The viewpoint of Bolognesi *et al.*^{31,32} regarding the orientation of polythiophene **17** molecules in the monolayer is also unclear. They consider that the main chain is parallel to the surface of water, the side chain is almost perpendicular to this surface, while the oxygen atom (at the free end of this chain) contacts water. Obviously, the latter two orientations cannot exist simultaneously.

In the case of the polymer **17**, both Y-transfer to a hydrophobic support and Z-transfer to a hydrophilic surface were carried out. In the former case, the transfer ratios were 0.9↑ and 0.8↓ (the arrow indicates the direction of support movement: ↑ means upwards from the subphase, while ↓ means downwards to the subphase) for the first 8–10 cycles, while in the latter case they were 1↑ and 0.2–0.5↓ for the first 12–14 cycles. The transfer ratio decreased as the number of cycles increased. A ten-layer LB film of polythiophene **17** was analysed by optical spectroscopy in combination with a cast film. The difference in positions of the absorption maxima for the LB film ($\lambda_{\text{max}} = 472$ nm) and for the film obtained from solution ($\lambda_{\text{max}} = 460$ nm) is explained by a

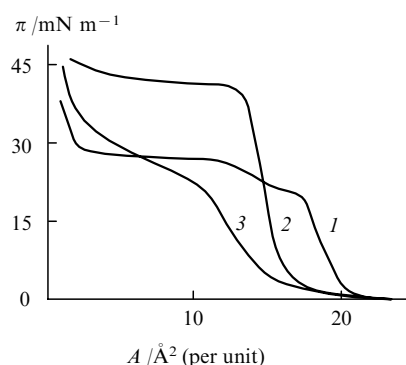


Figure 7. Compression isotherms of monolayers of polythiophenes **16** (1), **17** (2) and **18** (3).³¹

larger conjugation length in the case of the LB film. IR spectroscopy was used to demonstrate the higher planarity of the main polythiophene chain in the LB film. Similar data were also obtained for the polymer **16**.³³ These data differed from those of Callender *et al.*²⁸ who had also used optical spectroscopy but did not find differences between the spectra of LB films and those of a solution of polythiophene **15**. The discrepancy between the data obtained by both research groups were explained³¹ by the absence of a spacer in the side group of the polymer **15** between the thiophene ring and the oxygen atom. The ordered structure of polythiophene **17** in LB films was confirmed by polarisation optical spectroscopy and by electron microscopy.³² In addition, alternating LB films containing monolayers of **17** and cadmium alkadiynoate were obtained. Polymerisation of the diacetylene was carried out after transferring the monomer onto a solid support.³² It was shown that polymerisation does not result in destruction of polythiophene, and the spectrum of the Langmuir–Blodgett hetero-film does not show a shift of the exciton band of polydiacetylene, indicating the absence of interactions between the polydiacetylene exciton and the polythiophene macromolecules.

Thus, incorporation of ether groups in the side chain of polythiophene enhances the stability of monolayers in comparison with that of poly(3-alkylthiophenes). However, the problem of orientation of monomeric units both in monolayers and in LB films requires a more thorough analysis.

An increase in the polarity of monomeric units of polythiophene by incorporation of an ester group at position 3 enhances polymer spreading in comparison with that of polyalkylthiophene and polythiophene containing ether groups in the side chains.²⁴ Figure 8 presents the plots of surface pressure *vs.* the monomeric unit area for poly[3-(2-propanoyloxyethyl)thiophene] (**19**), poly[3-(2-decanoyloxyethyl)thiophene] (**20**) and, for comparison, poly(3-octylthiophene) (**11**). The short polar side chain in compound **19** 'stacks' the thiophene ring parallel to the surface of water: the limiting area per residue in this region is $\sim 28 \text{ \AA}^2$. Further, the rings are detached from the surface and the increase in pressure is observed in the region of closest packing of vertically arranged thiophene rings. The more complex isotherm shape in the case of polythiophene **20** monolayer is explained by the contribution of the comparatively long hydrocarbon chain arranged so that the polar group in each monomeric unit faces the water surface. The first inflexion on the isotherm results from detachment of these chains from the subphase surface. Although the monolayers of compounds **19** and **20** are stable, Kim *et al.*²⁴ were unable to transfer them onto solid substrates and to obtain LB films. This problem was solved for mixed monolayers of these polythiophenes with octadecylamine (see below).

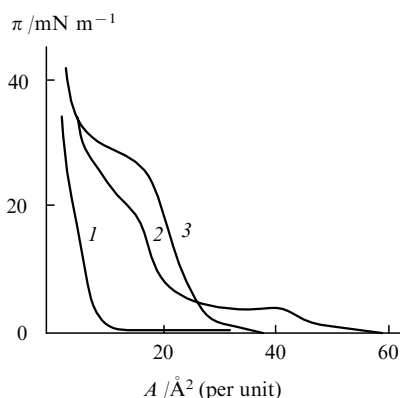
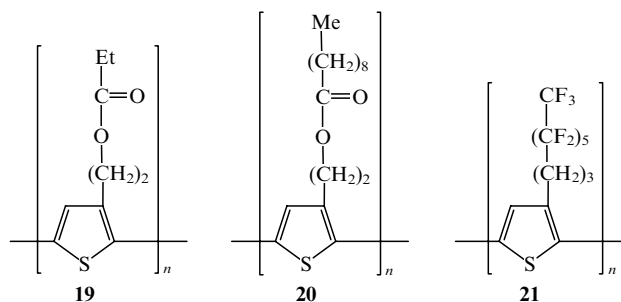


Figure 8. Compression isotherms of monolayers of polythiophenes **11** (1), **20** (2) and **19** (3).²⁴



The possibility of an increase in the polarity (hydrophilicity) of the side chains of polyalkylthiophenes for enhancement of the stability of monolayers has already been considered. However, the same result can be achieved by means of a considerable increase in the hydrophobicity of the side chain, as was demonstrated by Robitaille *et al.*³⁴ for poly[3-(4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl)thiophene] (**21**). Monolayers on the surface of water were from a solution of the polymer **21** in octafluorotoluene. The compression isotherm of polythiophene **21** at 9°C presented in Fig. 9 was obtained after several preliminary 'compression–expansion' cycles in the surface pressure range from 0 to 25 mN m^{-1} . Extrapolation of the curve to $\pi = 0$ gives the limiting area per residue of $34 \text{ \AA}^2$, which agrees with the area occupied by a fluorinated fatty acid molecule in the monolayer. The thermochromic properties of polythiophene **21** were studied using its LB films obtained at $\pi = 10, 14$ and 18 mN m^{-1} . Unfortunately, good LB films were not formed under these conditions: the transfer ratio onto silanised glass was ~ 0.6 . Transfer did not occur at all when the support moved to the subphase. Figure 10 shows the temperature dependences of optical absorption in the UV and visible spectral regions for the monolayer and a film obtained from solution on a rotating support. Robitaille *et al.*³⁴ believe with good reason that comparison of spectra of the two samples makes it possible to understand the nature of the thermochromism of compound **21**. Heating of the samples shifts the absorption maximum at 488 nm to 396 nm . It is believed^{35,36} that this optical effect results from conformational transition of the main polymer chain. It should be noted that the spectra for the two- (monolayer) and three-dimensional (film from solution) states of polythiophene **21** virtually coincide: in both cases, a coplanar structure existing at low temperature is transformed to a non-planar one at high temperature. Since the effects for the two- and three-dimensional systems are identical (Fig. 10a and b), it is concluded that this thermally induced conformational transition is determined by the polythiophene chain itself and does not depend on interchain interactions. However, it should be taken into account that this conformational transition is possible only if it is not prohibited by steric hindrance from the substituents at position 3. In the case of polythiophene incorporating rather

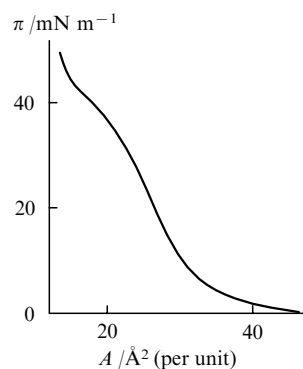


Figure 9. Compression isotherm of fluorinated polythiophene **21** at 9°C .³⁴

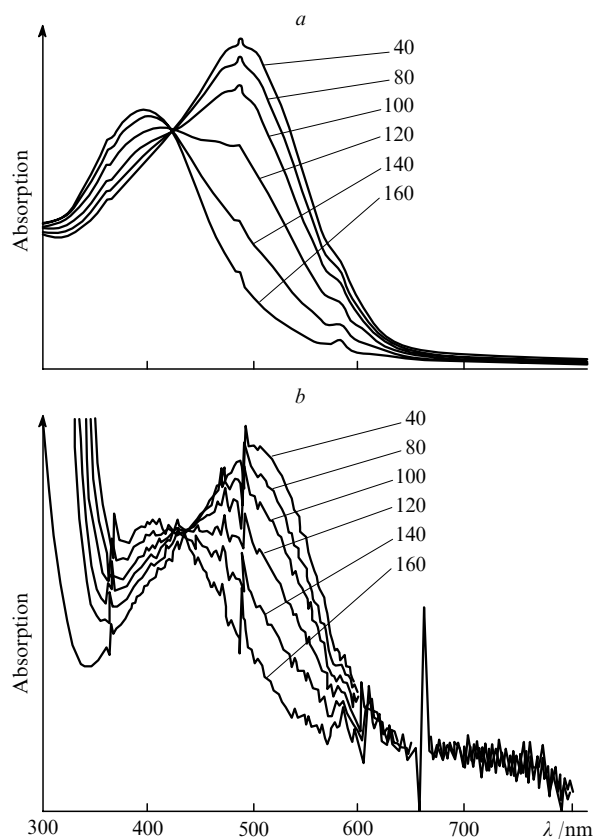
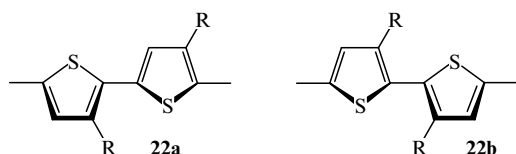


Figure 10. Absorption spectra of a monolayer (a) and a coating obtained from solution (b) of fluorinated polythiophene **21** at various temperatures.³⁴

The numbers at the curves indicate the temperatures (°C).

bulky side chains, such a transition is possible only if regioregular regions exist in the polymer ('head-to-tail' diads); however, the existence of such regions was not reported.³⁴

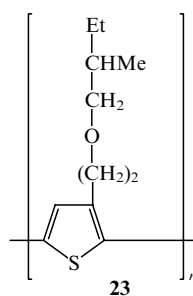
The problem of the regioregularity of poly(3-R-thiophenes), including the formation of stable molecular ensembles on liquid and solid supports, has made progress only in recent years after poly(3-R-thiophenes) with regioregularity of up to 100% had been synthesised and their study had begun.^{37–44} Two conformations of poly(3-alkylthiophene) are shown below: coplanar ('head-to-tail') (**22a**) and twisted ('head-to-head') (**22b**).



As shown by McCullough *et al.*,^{41–43} an increase in the regioregularity of poly(3-alkylthiophene) increases considerably the electric conductivity of the films and results in greater changes in the physical parameters of the polymers than for the samples synthesised with the use of the standard chemical or electrochemical polymer oxidation procedures. Similar conclusions were drawn^{39,40} in studies of the photoluminescence of poly(3-hexylthiophene) films with different regioregularity obtained from solutions. Obviously, the use of such an efficient organisation method as the Langmuir–Blodgett technique for obtaining ultra-thin films of structurally uniform poly(3-R-thiophenes) will make it possible to increase their uniformity and improve the parameters of various devices constructed from these films.

Ochiai *et al.*⁴⁵ compared the properties of monolayers of regioregular poly(3-{2-[(S)-2-methylbutoxy]ethyl}thiophene) (**23**) containing more than 93% of 'head-to-tail' conformers

(**23a**, $M_w = 2.5 \times 10^4$) and polythiophene containing as little as 46% of 'head-to-head' conformers (**23b**, $M_w = 2.05 \times 10^4$).



A monolayer of compound **23a** forms a condensed phase with a collapse surface pressure of $\sim 18 \text{ mN m}^{-1}$ (Fig. 11). The limiting area per residue is $17 \text{ \AA}^2$, which corresponds to an almost perpendicular arrangement of thiophene rings with respect to the surface; the head groups of these rings are oriented towards the subphase. A monolayer of compound **23b** has a larger limiting area per residue ($19 \text{ \AA}^2$), but the low collapse pressure of this monolayer ($\sim 10 \text{ mN m}^{-1}$) indicates its low stability and random orientation of the molecules. Due to these characteristics of monolayers of **23b**, they do not form LB films. Analysis of the polarised optical spectra in the region of 400–650 nm for LB films of the polymer **23a** showed that its molecules are oriented parallel to the surface of the substrate and the chain orientation correlates with the direction of movement of the support when the monolayers are transferred. Comparison of these spectra with those for films deposited from solution showed that in the case of LB films the molecules have a higher degree of orientation and larger conjugation lengths. This increases the lateral conductivity of polythiophene **23a** LB films doped with NOPF₆ or FeCl₃ to $1\text{--}5 \text{ S cm}^{-1}$, which is 4 to 5 orders higher than the conductivity of polythiophene **23b** films obtained from solution. In addition, LB films of the polymer **23a** have anisotropy of lateral conductivity and high cubic susceptibility.⁴⁵

Unfortunately, there are as yet few studies of this kind within the Langmuir–Blodgett method, and for individual polythiophenes only the studies cited above are available. Solutions, films obtained from solution, and solid polythiophenes are being studied thoroughly. These systems are not covered in the present review dealing with monolayers and LB films; however, we have to dwell on some general issues of the relationship between the structure, composition and properties of polythiophenes in solutions and in the bulk.

It is known⁴⁶ that electrochemical synthesis of poly(3-alkylthiophenes) gives units with substituents at positions 2 and 4, whereas chemical synthesis results in residues with substituents at positions 2 and 5. Both methods give irregular polymers. Naturally, these 'defects' affect the planarity of the main polymer chain

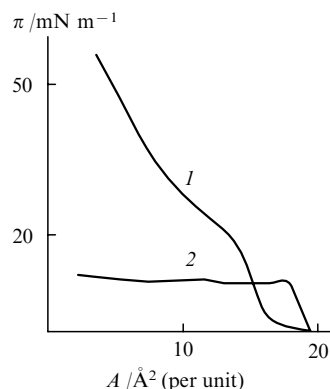


Figure 11. Compression isotherms of monolayers of polythiophenes **23a** (1) and **23b** (2) at 10°C .⁴⁵

and hinder both the intrachain and the interchain transport of charge carriers. As a result, poly(3,4-dialkylthiophenes) and poly(3,3'-dihexyl-2,2'-dithiophenes) mostly containing 'head-to-head' conformers have a small conjugation length and low conductivity.^{47,48} There are prerequisites for increasing the polymer regularity by polymerisation of long-chain 3-alkylthiophenes.^{49,50} However, in this case the polymer contains structural defects as well⁴⁸ [C(2)–C(4') bonds and branchings]. It is believed^{51,52} that regular polymers with high conductivities can be obtained from 3,4-disubstituted thiophenes if steric hindrance is removed. This assumption was checked⁵⁰ by the synthesis of poly(3-alkoxythiophenes), poly(3-alkoxy-4-methylthiophenes) and poly(3,4-dialkoxythiophenes) by chemical oxidation of monomers with anhydrous FeCl₃ (see Refs 48, 53). The effects of the position, size and nature of substituents on the molecular mass, positions of characteristic absorption bands and conductivities of the resulting polymers were determined. It was shown that the absorption band of 3,4-disubstituted polyalkylthiophenes is strongly (by ~200 nm) shifted towards the blue region in comparison with the bands of the other polythiophenes synthesised. This implies a non-planar conformation of chains due to strong steric interactions between the substituents and the main chain. As a result, gaps remain between the conjugated chains of the adjacent molecules; these gaps decrease the probability of charge carrier transfer according to the hopping mechanism.⁵² Replacement of alkyls by alkoxy groups in poly(3,4-dialkylthiophenes) increases considerably the conjugation length and conductivity of the polymer, which is explained by the smaller van der Waals radius of the oxygen atom (1.4 Å) in comparison with the methylene group radius (2.0 Å). This conclusion can be very important in the synthesis of Langmuir monolayers, since incorporation of a polar group enhances the ability of polythiophenes to spread over an aqueous subphase surface.

Studies on the synthesis of regular polythiophenes with various quantitative and qualitative compositions of substituents and their use for obtaining monolayers and LB films are already under way. For example, works have been published on the synthesis and properties of polythiophenes, polybithiophenes and polyterthiophenes containing such substituents as 3-cyclohexyl, 3-methyl-4-cyclohexyl, 3-alkylphenyl, *etc.*^{54–57}

IV. Mixed monolayers and Langmuir–Blodgett films of oligo- and polythiophenes

Analysis of the behaviour of monolayers and LB films of simple oligo- and polythiophenes showed that the formation of stable films on the surface of water requires adjustment of the hydrophilic-lipophilic balance of thiophenes towards enhancement of the hydrophilicity of the head group. In addition, a side group, most commonly an alkoxy group, is to be introduced into each thiophene ring of the main chain (in most cases, at position 3) in order to weaken the interchain interactions responsible for aggregation of macromolecules on the surface of water and incomplete spreading of the compound to form a monolayer. An easier method to obtain stable monolayers containing polythiophenes involves formation of mixed monolayers with an amphiphilic compound which forms stable monolayers with high collapse pressure. The problem of the role of intra- and interchain charge transfer is solved using mixed monolayers of conjugated polymers with compounds which are inert with respect to electric conductivity (fatty acids, alcohols, polymers). Obviously, incorporation of an inert component should not hinder the interchain charge transfer in the case of mixed films.

A five-membered oligomer of thiophene **1** ($n = 3$, S₅) was mixed with stearic acid²⁹ or eicosanoic acid⁵⁸ and placed on the surface of aqueous solutions containing CdCl₂. Compression isotherms obtained for monolayers of mixtures with different component ratios were used to determine the limiting area per molecule of oligothiophene S₅, which was 26 Å² for mixtures of S₅ with stearic acid²⁹ and 19 Å² for mixtures of S₅ with eicosanoic

acid.⁵⁸ Such a large difference was explained by the higher pH used in the former study²⁹ and better correspondence between the lengths of the molecules of S₅ and cadmium stearate (25.8 Å) than of S₅ and cadmium eicosanoate (28 Å). According to calculations,²⁹ the area of an S₅ molecule arranged at a right angle to the film surface and having a dihedral angle of 90° is 28 Å². Therefore, the area per S₅ molecule equal to 26 Å² should correspond to vertical orientation of oligothiophene with the dihedral angle ranging between 20° and 50°.

Figure 12 shows the dependence of the specific electric conductivity of iodine-doped LB films obtained from a mixture of S₅ and stearic acid (the content of S₅ was 30 mol.%) on the number of layers (N) in a Y type film.²⁹ One can see that for $N \leq 7$, the conductivity increases rapidly and reaches a steady-state value of

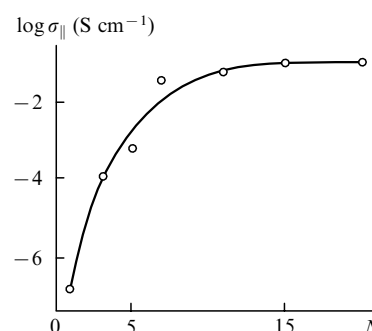


Figure 12. Dependence of the lateral conductivity on the number of layers in an LB film obtained from a mixture of oligothiophene **1** (S₅) (30 mol.%) and stearic acid.²⁹

0.1 S cm⁻¹ at $N > 15$. The dependences of the lateral conductivity on the mole fraction of S₅ in the mixture for 1-, 3- and 11-layer, iodine-doped LB films are presented in Fig. 13. Two regions are observed in the curves. For the 11-layer LB film, the conductivity reaches a plateau at a mole fraction [S₅] ≥ 0.35. The limiting conductivity (0.2 S cm⁻¹) corresponds to σ_{||} for iodine-doped bulk polythiophene (0.01–0.1 S cm⁻¹)⁵⁹ and exceeds the σ_{||} for the spray-deposited, iodine-doped S₅ film. The lateral conductivity of non-doped LB films does not exceed 10⁻⁹ S cm⁻¹, while the transverse conductivity σ_⊥ is lower than 10⁻¹² S cm⁻¹. The maximum conductivity can be reached by doping for a period of two days. The doping process is partially reversible: for the 21-layer LB film obtained from a mixture of S₅ with stearic acid (1 : 1), σ_{||} and σ_⊥ were 3.0 × 10⁻³ and 1.5 × 10⁻⁷ S cm⁻¹, respectively, after removal of iodine.

Since neither the oligothiophene chain length nor the film ordering affect noticeably the electric conductivity of oligomers

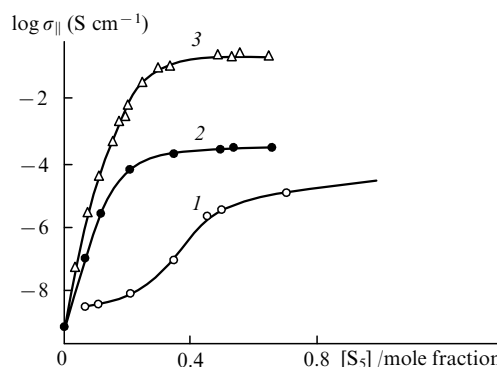


Figure 13. Dependence of the lateral conductivity of LB films consisting of monolayers of oligothiophene **1** (S₅) and stearic acid on the mole fraction of S₅ for an LB film containing 1 (*1*), 3 (*2*) and 11 layers (*3*).²⁹

doped with iodine,²⁹ it was concluded that the electric conductivity of polymers and oligomer ensembles is determined by the intermolecular transfer of charge carriers.

There are many more studies of mixed monolayers and LB films containing polythiophenes than of those dealing with monolayers of oligothiophenes and films of individual compounds. It is believed⁶⁰ that pure poly(3-alkylthiophenes) are unsuitable for obtaining organised ensembles for at least two reasons. First, they do not form true monolayers; when they spread over the surface of water, they form islets visible by naked eye. The same situation is observed for poly(3-alkylthiophenes) containing up to 18 carbon atoms in the side chain. Second, monolayers can be transferred onto solid supports only by the horizontal method. The films obtained in this manner have low degree of organisation. As in the case of oligothiophenes, these drawbacks can usually be overcome by using fatty acids such as stearic and eicosanoic acids.^{61–65}

Figure 14 shows the π - A plots for mixed monolayers with various compositions obtained from mixtures of poly(3-hexylthiophene) and stearic acid.⁶⁰ It is evident that the mixture containing up to 80 mol.% of the polymer (with respect to the repeating thiophene unit) forms a stable condensed monolayer. The phase transition in this monolayer is observed at high surface pressures (25 mN m⁻¹). For all component ratios, π increases with a decrease in the area until the transition region is reached where the surface pressure remains constant. A new abrupt increase in π starts at monolayer areas close to A for a monolayer of pure stearic acid. Obviously, the plateau corresponds to displacement of the polymer molecules from the liquid surface and formation of a bilayer film. This picture is observed for all alkyl-substituted polythiophenes except for poly(3-octadecylthiophene) in which strong interactions of the alkyl chains with the chains of similar length of stearic acid prevent polymer displacement from the interface.

Let us consider the properties of LB films obtained from these mixtures. The LB film thicknesses after one passage of the support through a mixed polythiophene–acid (2 : 1) monolayer at transfer pressures below (20 mN m⁻¹) and above (28 mN m⁻¹) the phase transition (plateau) were 32 and 44 Å, respectively (see Fig. 14). According to the optical spectroscopy data, the bilayer structure formed on the surface of water at high π is transferred onto the solid support. However, more precise X-ray diffraction data showed that the bilayer thickness in LB films correlates with the size of two stearic acid molecules and does not depend on the transfer pressure. The formation of high-quality LB films from a mixture of poly(3-hexylthiophene) with stearic acid was evidenced by linear dependences of the absorption intensity at the maximum of the characteristic absorption band of polythiophene on the

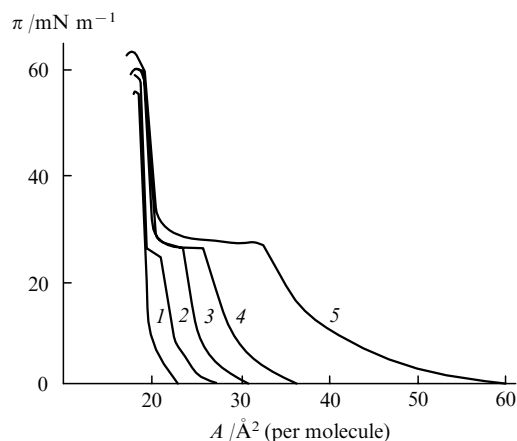


Figure 14. π - A Dependences for mixed monolayers of poly(3-hexylthiophene) and stearic acid for the molar component ratios: 0 : 1 (1); 1 : 2 (2); 1 : 1 (3); 2 : 1 (4) and 5 : 1 (5).⁶⁰

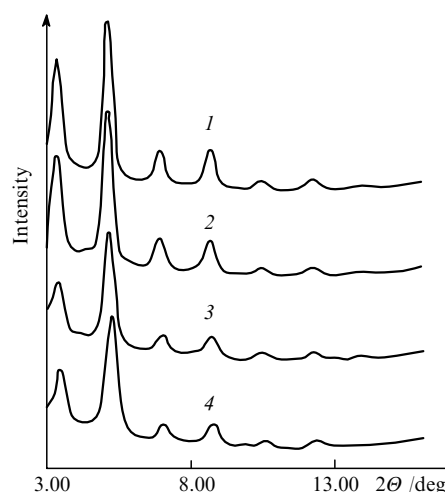


Figure 15. X-Ray diffraction diagrams for LB films consisting of mixed monolayers of poly(3-hexylthiophene) and stearic acid for the molar component ratios: 1 : 2 (1); 1 : 1 (2); 2 : 1 (3) and 5 : 1 (4).⁶⁰

number of layers for various component ratios and surface transfer pressures and by a linear relationship between the inverse capacity of LB films and the number of layers. The layered structure of LB films was confirmed by X-ray diffraction (Fig. 15). The X-ray diffractogram displays distinct Bragg peaks with an interlayer distance of 50 Å, which corresponds to a bilayer of stearic acid. Near-edge X-ray absorption fine structure analysis showed a high degree of organisation of stearic acid hydrocarbon chains in the bilayers and an irregular orientation of poly(3-hexylthiophene) chains. A model of a mixed LB film structure was built on the basis of the experimental data (Fig. 16).

The effect of the content of poly(3-octylthiophene) in a mixture with eicosanoic acid on the properties of monolayers and LB films was studied.⁶⁵ No plateau was found on the compression isotherms of monolayers (the mixture containing 60% of the polymer was an exception). As in other studies, an increase in the polymer fraction in the mixture resulted in an increase in the monolayer limiting area. The high stability of mixed monolayers [unlike the monolayers of pure poly(3-octylthiophene)] and the high surface collapse pressure (> 50 mN m⁻¹) made it possible to form a 45-layer LB film at a

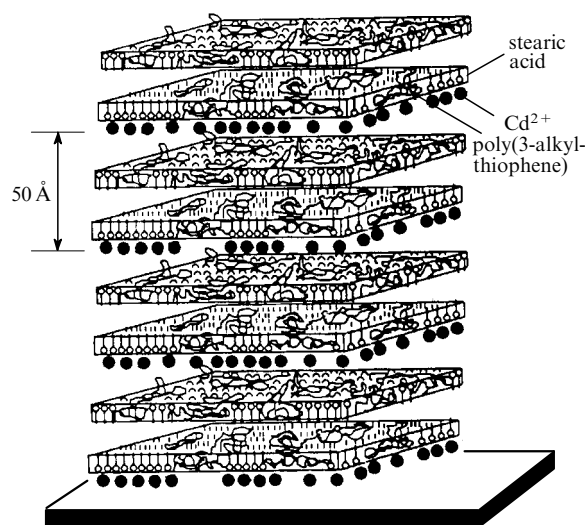


Figure 16. A model of the structure of an LB film obtained from a mixture of poly(3-hexylthiophene) and stearic acid.⁶⁰

transfer ratio close to 1. Despite the instability of pure poly(3-octylthiophene) monolayers, the respective LB films were obtained and their thicknesses were determined by ellipsometry. The thickness of one layer in an LB film was 40 Å, which is 3 Å thicker than that of one monolayer in the LB film obtained from a mixture of eicosanoic acid and poly(3-octylthiophene) measured by the same method. These data were not discussed, but it is easy to understand the origin of the larger thickness of the pure polythiophene LB film if its 'monolayers' were transferred at area per unit parameters insignificantly in excess of 5 Å². It should be noted that the thickness of one LB film layer of pure poly(3-octylthiophene) and its mixtures with eicosanoic acid specified above is considerably larger than the thickness of a densely packed monolayer of eicosanoic acid. In addition, ellipsometry, unlike X-ray diffraction, does not allow determination of the structure spacing parameters and hence does not provide data on the film layered structure. Such data were reported.^{60,66} It was found for mixed LB films of stearic acid with poly(3-hexylthiophene) in the ratios from 2:1 to 1:5 that the structure spacing corresponded to the thickness of a stearic acid bilayer.⁶⁰ It was also found for LB films obtained from binary mixtures (1:10 and 1:3) of poly(3-heptylthiophene), poly(3-decylthiophene) or poly(3-undecylthiophene) with cadmium eicosanoate that the structure spacing of all three systems corresponds to the thickness of a cadmium eicosanoate bilayer (55.2 Å).⁶⁶ Two reflections were observed for rather high contents of poly(3-decylthiophene) in a mixture with cadmium eicosanoate (3:1); these reflections corresponded to interlayer distances of ~70 and ~50 Å. This result and the broadening of the diffraction bands indicated a decrease in the system ordering. Despite the high content of behenic acid in a mixed monolayer with poly(3-hexadecylthiophene) (5:1 w/w) and its high stability ($\pi_c = 60 \text{ mN m}^{-1}$ and $A_0 = 13.7 \text{ Å}^2$ per unit), only a Z-type LB film (20 layers) could be obtained.⁶⁷ It was found in a study of these films by attenuated total internal reflection IR spectroscopy and reflection at grazing light angles that the LB film obtained from a mixture has a less organised structure than the LB film of pure behenic acid.

Mixed monolayers of poly(3-octylthiophene) and unsaturated oleic acid having the same hydrocarbon chain length as stearic acid were studied.⁶⁸ It was shown that an increase in the content of polythiophene in the mixture from 10% to 90% decreased the mean molecular area of the monolayer upon its destruction from 42 to 5 Å². Let us remind that in the case of saturated acids, the monolayer area generally increases with an increase in the polymer fraction.^{60,69} Exposure of the solution used for the formation of mixed monolayers of oleic acid and poly(3-octylthiophene) to daylight shifted the dependence of the monolayer area on the polymer content towards larger areas. The shoulder at 590 nm found⁶⁸ in the absorption spectra of LB films composed of mixed monolayers is explained by the formation of a charge-transfer complex between oleic acid and the thiophene rings.

The study of mixed monolayers of poly(3-butylthiophene) and stearic acid,⁷⁰ like yet another study⁶⁵ of the poly(3-octylthiophene)–eicosanoic acid system, did not show a plateau on the compression isotherms for the polymers with molecular masses differing by an order of magnitude (2.5×10^5 and 1.5×10^4). For these systems, as for the majority of other mixtures of fatty acids with polythiophenes, the area per monomer unit in a monolayer increases with an increase in the polymer content in the mixture.⁶⁵ The main differences in the shape of the compression isotherms for polythiophene samples with different molecular masses were observed in the region of destruction of mixed monolayers, *i.e.* in the transition from a two-dimensional to a three-dimensional state of the material. The surface potential of monolayers is 'insensitive' to these differences and to the obvious differences of the aggregation states of polymer monolayers with significantly different molecular masses. In both cases (as for the majority of monolayers of low- and high-molecular-mass compounds), the surface potential starts to increase at monolayer areas considerably exceeding those where the increase in the surface pressure starts. The transfer

of mixed monolayers onto a glass surface by the vertical method was studied in detail;⁷⁰ it was found that the transfer ratio is close to unity and that the resulting LB films of the Y type have homogeneous structures.

It was noted above that important information on the properties of conjugated systems can be obtained from absorption spectra of LB films and their comparison with the spectra of polymers in solutions. High quality LB films of the Y type with various ratios of stearic acid and poly(3-hexylthiophene) were described.⁶⁰ Differences between the absorption spectra of LB films of individual polythiophenes **16** and **17** and their films obtained from solution were observed;^{31–33} however, no differences were found between similar spectra of LB films obtained from a mixture with stearic acid and that of a film obtained from a solution of pure poly(3-hexylthiophene).^{60,69,70}

The position of the $\pi-\pi^*$ -transition maximum in the absorption spectra of LB films consisting of mixed monolayers of poly(3-alkylthiophenes) and cadmium eicosanoate depends on the length of the polymer alkyl chain.⁶⁶ For example, for LB films of poly(3-decylthiophene) and poly(3-undecylthiophene), the absorption maximum of a 1:3 polymer:salt mixture was observed at 520 and 515 nm, respectively, whereas in the case of a film obtained from solution, the absorption maxima were at 477 and 500 nm. For poly(3-heptylthiophene), no differences between the absorption spectra of mixed LB films and a film formed from solution were found. These data are believed⁶⁶ to be consistent with other data.^{60,71} It was therefore concluded that the conjugation length in poly(3-decylthiophene) and poly(3-undecylthiophene) is larger in LB films than in films formed from solution. This effect was explained by interactions between the hydrocarbon chains of the acid and poly(3-alkylthiophenes). For poly(3-heptylthiophene), no increase in the conjugation length in LB films was observed.

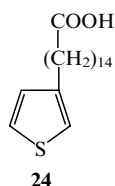
The absorption spectra of LB films containing poly(3-octylthiophene) and eicosanoic acid displayed a red shift of the absorption band maximum by 60 nm in comparison with the position of the absorption band maximum of a solution of the polymer in chloroform.⁶⁵ As in yet another study,³⁶ this effect was explained by conformational reorganisation of the chain in LB films. Ageing of the film shifted this absorption band towards the short-wave region. Doping of LB films was carried out in SbCl₅ or iodine vapour. As a result, the LB film colour changed from red to blue, while the conductivity increased from 2×10^{-9} to $2 \times 10^{-5} \text{ S cm}^{-1}$ for iodine and to $1 \times 10^{-4} \text{ S cm}^{-1}$ for SbCl₅.⁶⁵

The conductivity of a mixed 34-layer LB film doped with nitrosyl hexafluorophosphate depends on the component ratio.⁶⁰ An increase in the poly(3-hexylthiophene) content in a mixture with stearic acid from 1:2 to 5:1 increases the electrical conductivity from 0.02 to 2.0 S cm⁻¹. Similar results were obtained⁷² for LB films consisting of binary mixed monolayers (2:1) of stearic acid with poly(3-butylthiophene), poly(3-octylthiophene) or poly(3-octadecylthiophene); the maximum electric conductivity was 5.0 S cm⁻¹. Doping also results in significant changes in the absorption spectra of mixed LB films. The intensity of the strong absorption band corresponding to $\pi-\pi^*$ -transition of the conjugated main chain ($\lambda_{\text{max}} = 500 \text{ nm}$) decreases considerably and two new bands appear at 800 and 2200 nm, which correspond to transitions between the valence band and the new bipolar charged states that appear due to doping.⁷³

Attempts to incorporate ions in mixed LB films consisting of poly(3-octylthiophene) with stearic acid (1.4:1) were made in order to increase the conductivity of these films.⁶⁹ However, even small contents of *e.g.*, N⁺ (5×10^{14} ions per cm²) violated the LB film layer structure, apparently due to destruction of stearic acid. The conductivity increased to only $10^{-3} \text{ S cm}^{-1}$ with increase in the N⁺ content by 2 orders of magnitude and resulted from formation of a conducting form of carbon. This not only destroyed completely the layer structure of the film but also destroyed the conjugated polymer structure (optical spectroscopy data).

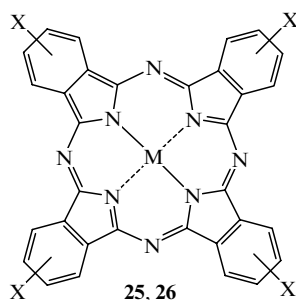
Mixed monolayers and LB films of poly(3-hexylthiophene) or poly(3-dodecylthiophene) with poly(isobutyl methacrylate) were studied.⁷¹ Taking account of the deviation from linearity of the relationship between the monolayer limiting area and composition, it was concluded in this study that polyalkylthiophenes and poly(isobutyl methacrylate) are compatible. Comparison of the optical spectra of mixed LB films with those of films with the same component ratio cast from solution showed that the conjugation efficiency for LB films containing poly(3-dodecylthiophene) is higher than for cast films but it is lower for films containing poly(3-hexylthiophene). The aggregation states of macromolecules are also different for these two film types. The conductivity of mixed LB films doped with sulfuric acid ranged from 0.05 to 0.1 S cm⁻¹; doping changed the LB film colour from red to blue.

Polymerisation of thiophenes can occur in organised planar systems, resulting in the formation of anisotropic macromolecules.⁷⁴ In view of this, the properties of pure thiophene **24** and its mixtures with viologen were studied.⁷⁵



It was shown by X-ray photoelectron spectroscopy with angular resolution^{76–78} that an LB film of compound **24** has a layered structure (bilayers of the Y type) with a distance of 4.6 nm between the thiophene sublayers. In mixed monolayers and in LB films containing thiophene **24**, phase separation does not occur due to interactions between the positive charges of viologen and the deprotonated carboxyls of thiophene resulting in donor-acceptor diads.

In addition to mixed monolayers and LB films of polythiophenes with insulating molecules (mostly, fatty acids), of significant interest are thin planar systems consisting of mixtures of a conducting polythiophene with a conducting compound manifesting a surfactant property in an aqueous medium. Rikukawa *et al.*⁷⁹ used mixed monolayers of poly(3-hexylthiophene) with nickel (**25**) and iron (**26**) tetra-*tert*-butylphthalocyanines.



M = Ni (**25**), Fe (**26**); X = Bu^t.

It is considered^{80, 81} that, along with unique electrical properties, phthalocyanines have an important advantage of higher stability of their monolayers in comparison with the stability of monolayers of fatty acids. The behaviour of pure phthalocyanine monolayers is essentially different: the limiting area of a phthalocyanine **26** monolayer is 75 and that of phthalocyanine **25** monolayer is only 34 Å² per molecule. In the former case, the molecular planes are oriented perpendicularly to the surface of water, and in the latter case the monolayer consists of aggregates whose thickness exceeds the size of one molecule. Incorporation of polythiophene expands slightly the monolayer of compound **25** and increases considerably the area of the monolayer of compound **26**. Thus, in the latter case the compatibility of monolayer components was higher than in the former, and displacement of polythiophene molecules occurred with much greater difficulty.

The structural organisation of mixed monolayers and films on a solid substrate and the character of interactions between the components were determined more accurately by comparison of the optical spectra of two mixed LB films with the spectra of phthalocyanines in solution and with the spectra of mixed LB films of phthalocyanines with stearic acid. It was found that the sulfur atoms of the thiophene rings tend to coordinate with the iron atoms of phthalocyanine. This limits the possibility of formation of phthalocyanine dimers and trimers and increases the extent of molecular mixing. For mixed LB films of compound **25** with polythiophene (as with stearic acid), the interactions between the molecules are not so strong and aggregation of molecules of compound **25** is much stronger than that in mixed LB films containing compound **26**. Interesting results of structural studies of mixed films carried out by small-angle X-ray scattering and by optical spectroscopy were reported. In mixed LB films of phthalocyanine **25** with polythiophene, as in the LB films of pure compounds **25** and **26**, the majority of phthalocyanine molecules form one-dimensional linear structures in which the ring planes are oriented perpendicularly to the substrate surfaces. In mixed films of phthalocyanine **26** and polythiophene, the phthalocyanine molecules exist mainly as monomers and have random organisation because of interaction with the thiophene units. The conjugated polymer chains in both mixed films are oriented parallel to the film surface, while the side chains have no preferential orientation. It should be noted that irreversibility of thermochromic properties was reported only for mixed LB films of poly(3-hexylthiophene) with phthalocyanine **26**:⁷⁹ heating from 25 to 120 °C changed the colour of the film from dark brown to green. The absorption spectrum of the film changed correspondingly. It should be noted that mixed films with the same component ratio cast from solution on a solid substrate did not display thermochromic properties. Doping of mixed LB films was carried out in iodine and SbCl₅ vapours.⁷⁹ As a result, electrical conductivity increased in comparison with the electrical conductivity of the LB films of pure phthalocyanines (10⁻⁵–10⁻⁶ S cm⁻¹) by several orders and reached 10⁻¹–10⁻² S cm⁻¹. Unlike LB films doped with iodine, the films doped with SbCl₅ were stable in vacuo and in an atmosphere of nitrogen. According to optical spectroscopic data, both components of the mixed film underwent doping. Figure 17 shows the dependences of the lateral conductivity of mixed LB films on the content of polythiophene components. It is evident that the maximum conductivity is reached at 80 mol.% of the polymer in the mixture; the conductivity of the system with phthalocyanine **26** is by an order of magnitude higher than that for the systems with phthalocyanine **25**. This effect is explained by coordination between the molecules of polythiophene and iron phthalocyanine.

Of considerable interest are the alternating Langmuir–Blodgett heterofilms consisting of materials with different conductivity band widths. These films are convenient models of quantum wells in organic systems.^{82, 83} In addition, these alternating systems can be used for studies of energy transfer in

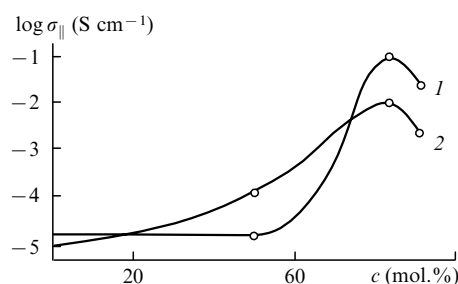


Figure 17. Dependence of the lateral conductivity of SbCl₅-doped Langmuir–Blodgett films consisting of mixed monolayers of poly(3-hexylthiophene) and iron (**1**) and nickel (**2**) phthalocyanines on the polymer content (*c*).⁷⁹

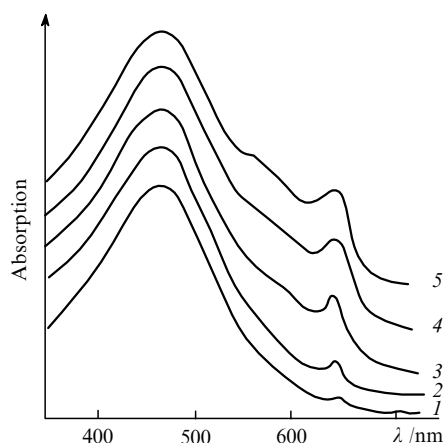


Figure 18. Absorption spectra of an alternating Langmuir–Blodgett film obtained from a mixture of polythiophene **17** and alkadiynoic acid at different irradiation times (light with the wavelength of 254 nm).³² Time /min: (1) 0.25; (2) 2; (3) 12; (4) 24; (5) 56.

polymeric materials. For this purpose, Bolognesi *et al.*³² chose alternating mixed LB films consisting of poly(3-methoxydecylthiophene) **17** and cadmium salt of the alkadiynoic acid $\text{H}(\text{CH}_2)_{12}\text{C}\equiv\text{CC}\equiv\text{C}(\text{CH}_2)_8\text{COOH}$. UV irradiation of the LB films formed from a polymer: monomer mixture at a wave length of 254 nm gave a film that contained alternating layers of two conjugated polymers. Figure 18 shows the absorption spectrum of a Langmuir–Blodgett heterofilm for various irradiation times determining the degree of polymerisation of diacetylenic acid. The band at 640 nm corresponds to exciton absorption of the extended polydiacetylenic chain. The band at 540 nm overlapping with the neighbouring bands originates from absorption of short polydiacetylenic chains.⁸⁴ It should be noted that irradiation of the Langmuir–Blodgett heterofilm does not shift the polythiophene absorption band at 505 nm nor decreases its intensity. On the other hand, laser irradiation of the original heterofilm near the polythiophene absorption (488 nm; light with this wavelength does not cause polymerisation of pure diacetylenic acid or its salt) results not only in polymerisation of the amphiphilic diacetylene but also in a shift of the maximum of the polythiophene absorption band to higher energies and in a decrease in its intensity. This result suggests photooxidation of the polythiophene component of the hetero structure and its subsequent sensitising effect on the photopolymerisation of the diacetylene. The identity of the absorption spectra of Langmuir–Blodgett homo- and heterofilms containing polydiacetylene indicates the one-dimensional exciton nature in the structures of both films, *i.e.* the absence of interactions between the polydiacetylene exciton and the polythiophene macromolecules.³²

Mixed monolayers of poly(3-hexylthiophene) and pentacosanoic acid were studied by Tsumura *et al.*⁸⁵ Stable monolayers were obtained for various component ratios; after transferring them onto a solid substrate by the vertical method they were polymerised by exposure to light. It was found that polythiophene does not affect the polymerisation of the diacetylenic acid and the LB film has a layered structure with oriented molecules of both components; the area per molecule in the mixed monolayer and the structure spacing in the LB film indicate the formation of bilayer films.⁸⁵ In this LB film variant, the bilayer consists of identical mixed monolayers rather than of alternating monolayers of different polymers (as in the previous case).

A detailed study of the effect of thickness, temperature and electric field on the conductivity mechanism in LB films consisting of mixed (5:1) monolayers of poly(3-hexylthiophene) and 3-decanolpyrrole was carried out.⁶² The dependence of the lateral conductivity and charge mobility in external electric field for a non-doped LB films, an LB film doped with NOPF₆ and a

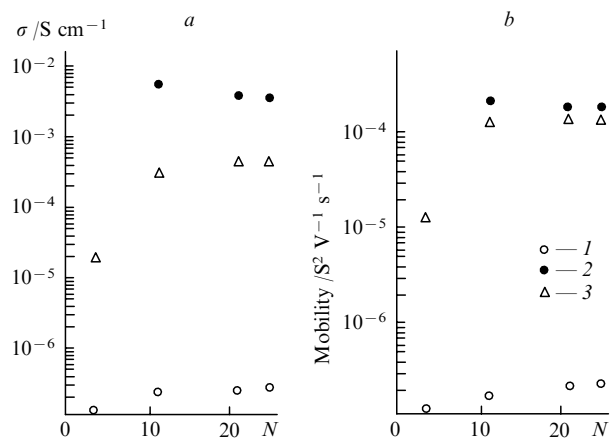


Figure 19. Dependences of specific electric conductivity (a) and charge mobility in electric field (b) for LB films consisting of mixed layers (5:1) of poly(3-hexylthiophene) and 3-octadecanoylpyrrole on the number of layers.⁶² Film: (1) non-doped; (2) doped with NOPF₆; (3) dedoped.

dedoped LB film (a sample which was allowed to relax after doping to a certain high conductivity) on the number of layers is presented in Fig. 19. It is evident that doping increases the conductivity by 5 orders of magnitude, while the mobility is increased by 4 orders. In view of this, a conclusion on the primary role of charge mobility in the LB film conductivity was drawn.⁶² The thickness of LB films has but an insignificant effect on these parameters, except for the region between the 3- and 11-layer LB films. The decrease in conductivity upon keeping the samples in air (preparation of the dedoped system) is due to the loss of activity of the PF₆[−] anions because of their reaction with moisture. Obviously, this affects the thinner film most strongly (see Fig. 19). It was shown in the same study that the dependence of conductivity (and charge mobility) on temperature for the non-doped film has the form $\log \sigma \sim T^{-1/4}$. This means that the hopping mechanism is the main mechanism of conductivity.⁸⁶ Based on this conclusion and on the experimental dependences of conductivity on external electric field, the mean hopping length and energy were calculated as 230 Å and 0.41 eV, respectively, using the Mott equation.⁸⁷

In the case of doped and dedoped samples, the temperature dependence of conductivity had the form $\log \sigma \sim T^{-1/4}$ (Fig. 20). Extrapolation of the straight line obtained for the doped LB films to room temperature gave a conductivity of 0.1 S cm^{−1}. After dedoping, the plot slope and hence the activation energy changed, but the dependences still remained linear. Similar relationships are observed in the case of metal and metal-ceramic systems consisting of grains;^{88,89} in view of this, some possible mechanisms describing the conductivity in these systems were considered.⁶² Based on comparative analysis, the conclusion was drawn that the tunnel mechanism with charge transfer operates in poly(3-alkylthiophene) films doped with NOPF₆ (see Ref. 90). It was established on the basis of these concepts that dedoping results in an increase in the size of conducting grains (domains) in LB films from 30 to 50 Å. The conducting domains are formed by the main conjugated polymer chains separated by the side alkyl groups. Interesting data on changes in the conductivity mechanism were obtained for 11-layer LB film samples exposed to external electric fields with field strengths up to 0.5 MV cm^{−1}. Transition to the Fowler–Nordheim tunnelling mechanism was observed in this case.^{91,92}

Analysis of the properties of monolayers and LB films of individual regioregular polythiophenes synthesised in recent years showed the advantages of these structurally homogeneous polymers assembled in organised planar ensembles over the systems

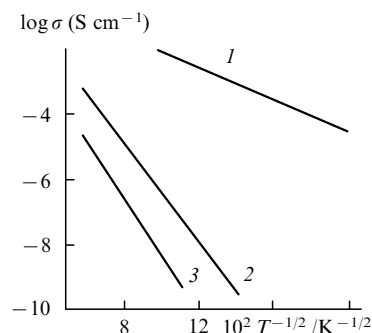


Figure 20. Temperature dependence of specific electric conductivity of a 25-layer LB film consisting of mixed (5 : 1) monolayers of poly(3-hexylthiophene) and 3-octadecanoylpyrrole.

Film: (1) non-doped; (2) moderately doped with NOPF₆; (3) dedoped.

containing poly(3-R-thiophenes) with random orientation of substituents.

The effect of the structural homogeneity of the polymer chain on the properties of monolayers and LB films also manifests itself in the case of mixed monolayers.⁹³ This is evident if one compares the compression isotherms of mixed monolayers of stearic acid with regioregular poly(3-hexylthiophene) containing up to 100% of 'head-to-tail' diads presented in Fig. 21 with the compression isotherms of a mixture of stearic acid with poly(3-hexylthiophene) having a random distribution of the chain substituents (see Fig. 14). Both monolayers consist of two phases, but the larger area and the smoother transitions between the phase states in the range of 20–30 mN m⁻¹ for the former monolayer (see Fig. 21) suggest the better compatibility of stearic acid with the regular polythiophene. A similar trend was observed⁹⁴ in a study of the effect of the chain length of the alkyl substituent in polythiophene on the behaviour of monolayers and LB films obtained from its mixture with stearic acid. Smoothing of compression isotherms in the phase change region observed for the mixture of fatty acid with poly(3-hexylthiophene) is explained by better compatibility in this system than in the system with shorter alkyl substituents in polythiophene.

The mixed monolayers of stearic acid with regioregular poly(3-hexylthiophene) were transferred by the horizontal method at a surface pressure of 20 mN m⁻¹ to give the Y type LB films (20 layers) on a hydrophobised glass plate surface.⁹³ It was shown by X-ray diffraction for LB films containing 2 : 1 polythiophene and stearic acid in monolayers that the film has a distinct layered structure with an interlayer distance of 17 Å. The same structure spacing found previously for poly(3-hexylthiophene) films cast from solution^{42,95} corresponds to the distance between the polymer chains stacked parallel to the substrate

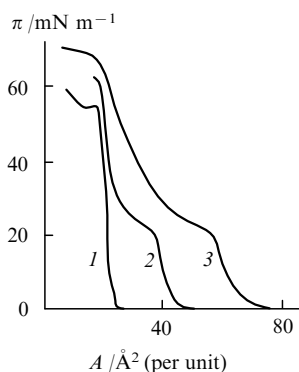


Figure 21. Compression isotherms of monolayers of regioregular poly(3-hexylthiophene) and stearic acid with component molar ratios of 0 : 1 (1); 2 : 1 (2); 5 : 1 (3).⁹³

surface. However, the interlayer distance determined by X-ray diffraction for LB films composed of mixed (1 : 2) monolayers of stearic acid and irregular poly(3-hexylthiophene) corresponded to a bilayer of cadmium stearate, *i.e.*, 50 Å.⁹⁶ Figure 16 illustrates the structure of such an LB film. No similar scheme for LB films consisting of stearic acid and regular poly(3-hexylthiophene) has been reported in the literature; however, it can be expected that the stearic acid molecules in this system either form a tilted phase or are distributed along the polythiophene chains.

Rikukawa *et al.*⁹³ compared the UV and visible absorption spectra for 2 : 1 mixtures of regioregular and irregular poly(3-hexylthiophene) and stearic acid. According to the spectra presented in Fig. 22, the π – π^* -transition energy of the mixture with the regular polymer is lower than that in the system with irregular polythiophene. This implies that the molecules of the former polythiophene in LB films have a more stretched structure and have a larger conjugation length than the molecule of the latter polythiophene. The lateral conductivity of LB films of mixed (5 : 1) monolayers of regioregular poly(3-hexylthiophene) with stearic acid doped with NOPF₆ was 50–100 S cm⁻¹, which is almost 1000 times higher than the lateral conductivity of a similar system containing irregular poly(3-hexylthiophene). It should be noted that the conductivity of LB films obtained from a mixture of regioregular poly(3-hexylthiophene) and stearic acid is several tens times higher than the conductivity of LB films obtained from the pure regioregular compound.⁴⁵

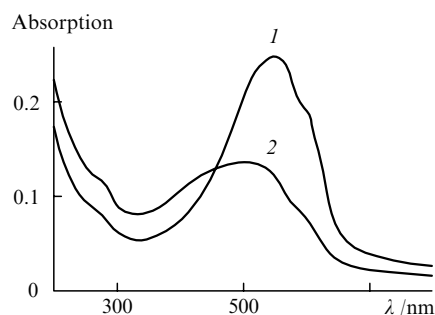


Figure 22. Absorption spectra of a 20-layer LB film consisting of mixed (2 : 1) monolayers of regioregular (1) and irregular (2) poly(3-hexylthiophene) and stearic acid.⁹³

Thus, the regioregularity of polythiophene favours an increase in compatibility of the polymer with stearic acid and results in a sharp increase in electric conductivity of thin films consisting of these components. These features of polythiophene can intensify the development of molecular devices. In addition, comparison of systems containing polythiophenes with different degrees of regularity enables deeper insight into the relationship between the structure and properties of conducting polymers.

V. Prospects for the application of polythiophene Langmuir–Blodgett films in molecular devices

It has been noted in many publications that LB films of polythiophenes and their mixtures with other substances can be used for practical purposes, nevertheless only a few works describing molecular devices based on these compounds are available.

The first study with mixed monolayers of oligothiophene **1** (S₅) with eicosanoic acid in a Langmuir–Blodgett heterofilm (alternating mixed monolayers and pure eicosanoic acid monolayers) was carried out as early as in 1974⁵⁸ (see footnote ‡). A cell was designed for photocurrent measurements, in which the LB film contained a mixed monolayer with oligothiophene S₅ located

‡ This was the first publication of Kuhn and his colleagues who laid the foundation of rapid development of studies in molecular design combined with the Langmuir–Blodgett technique.

close to one of the electrodes (aluminium or mercury) or at a certain distance set by the number of spacer monolayers of pure eicosanoic acid. By measuring the dependences of photocurrent on the applied voltage, temperature, and the arrangement of the conducting and insulating layers, the photophysical parameters of the device and the mechanism of generation of thermo- and photocurrent were determined. The authors suggested the main directions in the design of photoelectric devices. However, to date, scientific literature contains no information on the development of these kinds of devices based on polythiophene LB films. Nevertheless, metal–insulator–semiconductor transistors⁹⁷ and light-emitting devices^{39, 40, 55, 56, 98} suitable for inexpensive flat colour displays and adjustable lasers from oligo- or polythiophene films deposited from solution or spray-deposited on electrodes are being designed.

Ng *et al.*⁹⁹ used LB films of mixed monolayers of poly [3-(6-hydroxyhexyl)thiophene] (**27**) or poly(3-octylthio-2,2'-bithiophene) (**28**) and octadecanol as a sensor for heavy metal ions. A quartz crystal microbalance was used as the recording device. The high quality of the LB films obtained (up to 40 monolayers) was confirmed by the facts that the change in frequency of the quartz resonator depended linearly on the number of LB film layers and that the transfer ratio of monolayers was equal to unity.

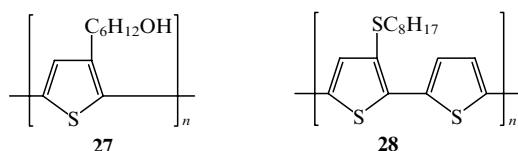


Figure 23 shows the dependence of adsorption of metal ions on a 10-layer LB film from mixed (3 : 1) polythiophene **27** : octadecanol monolayers deposited on the quartz resonator on the time of LB film exposure to 20 ppm solutions of ions at neutral pH and 25 °C. Similar results were obtained for mixed (1 : 3) polythiophene **28** : octadecanol LB films. One can see in the figure that the LB films of pure octadecanol does not adsorb metal ions under the same conditions. Complexing of metal ions with the polythiophene sulfur atoms is the driving force of adsorption. The selectivity in the series of ions $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Fe}^{2+}$ correlates with the ionisation potentials and ionic sizes in the Irving–Williams series. The higher adsorption of Ag^+ and Hg^{2+} in comparison with the other ions is explained by the high affinity of these ions to the sulfur atom. An important feature of the sensor is its reversibility: complete regeneration of the sensor upon exposure of the resonator with LB films in 1 mM ethylenediaminetetraacetic acid solution occurred in 5 min. An increase in the number of layers in the LB film increased the

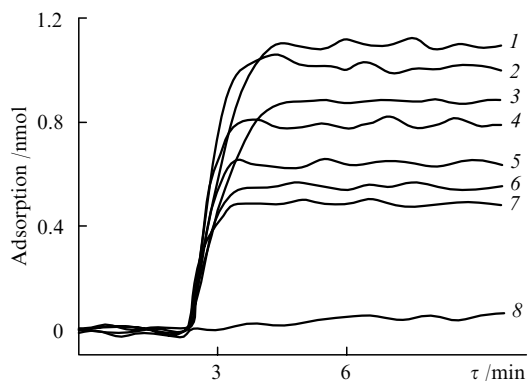


Figure 23. Dependence of the adsorption of metal ions on a 10-layer LB film consisting of mixed (3 : 1) polythiophene **27** : octadecanol monolayers on the time of exposure to solutions containing ions: Ag^+ (1); Cu^{2+} (2); Hg^{2+} (3); Ni^{2+} (4); Co^{2+} (5); Zn^{2+} (6); Fe^{2+} (7); Cu^{2+} + octadecanol LB film (8). The concentrations of the ions are 20 ppm (see Ref. 99).

absolute value of the change in the quartz resonator frequency Δf (the mass of the absorbed ions increases). This result indicates that the diffusion of ions in LB films does occur. However, for example, the 40-layer LB film was unstable and delaminated from the substrate after 7–10 measurements, whereas the 20-layer LB film withstood 50 measurements.

The concentration dependences of Δf for Ag^+ and Hg^{2+} ions are shown in Fig. 24. It is evident that a linear dependence is preserved up to the 100 ppm concentration. At higher concentrations, the frequency is unchanged because of saturation of the LB film with ions.

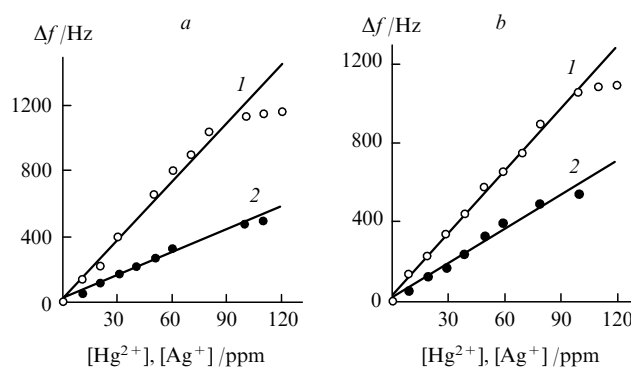


Figure 24. Concentration dependences of changes in the frequency of a quartz resonator with a 20-layer mixed LB film after exposure to a solution containing Hg^{2+} (1) and Ag^+ (2).

Film: (a) polythiophene **27** : octadecanol (3 : 1); (b) polythiophene **28** : octadecanol (1 : 3).⁹⁹

The time dependence (Fig. 25) shows the lower detection limit of Hg^{2+} ions by the 20-layer LB film. Adsorption where Δf exceeds the ‘noise’ (30 Hz) by a factor of three is chosen as the criterion. Each addition of Hg^{2+} ions with a concentration of 0.1 ppm to the solution where the resonator with the LB film is located produces a sharp change in the resonator frequency. The three changes in frequency shown in Fig. 25 corresponded to changes in the Hg^{2+} mass by 45, 38 and 36 ng. It was noted⁹⁹ that the sensor sensitivity can be increased at least twofold. The sensor selectivity was tested for the 5 ppm concentration of the Hg^{2+} ions. It was found that such cations as Na^+ , K^+ , Ca^{2+} , Pb^{2+} , Cr^{2+} , Co^{2+} and Ni^{2+} (but not Ag^+ and Cu^{2+}) interfere with the determination of Hg^{2+} if their concentrations in solution were twice as high as that of mercury. The same concentrations of anions such as CO_3^{2-} , ClO_4^- , SO_4^{2-} , PO_4^{3-} and Cl^- do not affect the

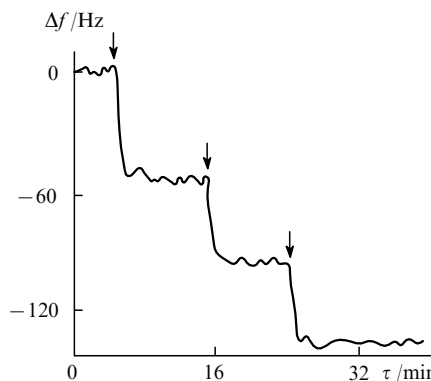


Figure 25. Dependence of the frequency of a quartz resonator with a 20-layer LB film consisting of mixed (3 : 1) polythiophene **27** : octadecanol monolayers on time of exposure in a solution containing Hg^{2+} . The arrows indicate the instants of addition of Hg^{2+} ions with a concentration of 0.1 ppm (see Ref. 99).

determination of Hg^{2+} , but anions such as Br^- , I^- , CrO_4^- and CNS^- form stable complexes with mercury. Thus, although the sensitivity and selectivity for many cations and anions are high, the problem of selectivity remains unsolved for a number of anions.

Mixed (1 : 1) binary monolayers of polythiophenes **11**, **19** and **20** and octadecylamine were studied with the purpose of obtaining a sensor for NO_2 .²⁴ The compression isotherms for the mixtures have the same character as those of the pure compounds but with lower compressibility and a considerably smaller difference in the monolayer areas; the π – A plot for polythiophene **11** is shifted to larger areas: the limiting monolayer area per thiophene unit increased from 9 to 20 Å². Figure 26 shows the dependences of quartz resonator frequency on the exposure time of a 14-layer LB film composed of mixed binary monolayers of polythiophenes **11**, **19** and **20** and octadecylamine in NO_2 (550 ppm). The differences in sensitivity of films containing the three polythiophenes cannot be caused by differences in the initial mass of the deposited substance as the monolayer areas corresponding to the surface pressure used for their transfer (30 mN m^{−1}) differed insignificantly. Taking into account the identity of the head groups of these compounds, one can state that the observed differences in sensitivity are caused by the side chains. Unfortunately, the sensor reversibility was low: treatment of the films in vacuo at 40 °C for one hour changed the frequency by no more than 10% (see Fig. 26).²⁴ NO_2 can be determined using a reported principle¹⁰⁰ for a gas sensor (for NO_2 , H_2S , NH_3 and others) in which a thin film (not LB film) of electropolymerised polythiophene is used as the working element. Changes in electrical resistance of this sensor upon exposure to NO_2 (an electron acceptor) occur due to chemical doping, whereas in the case of electron-donating gases (for example, H_2S), the resistance changes due to a decrease in the number of charge carriers in the polythiophene film.

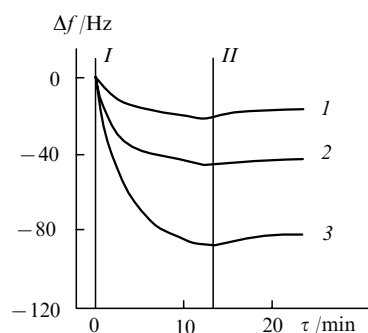


Figure 26. Dependence of frequency change on the time of exposure of a 14-layer LB film consisting of mixed (1 : 1) polythiophene : octadecylamine monolayers in NO_2 (550 ppm).²⁴ Polythiophene: (1) **20**; (2) **19**; (3) **11**. The vertical lines indicate the times of turning on (I) and off (II) the NO_2 generator.

VI. Conclusion

The above analysis of the properties of conducting polythiophenes in monolayers and LB films shows that these objects are of significant interest for theoretical study and for practical application. The solubility of polythiophenes in ordinary solvents and formation of rather stable monolayers in one-component systems and definitely stable layers in multicomponent systems (in mixtures with inert and reactive amphiphilic compounds) and their resistance against moisture and oxygen in the initial and doped states make these polymers superior to the known conjugated polymers (for example, polydiacetylene, polypyrrole, *etc.*). Incorporation of substituents at positions 3 or 3 and 4 of the thiophene monomer, control of the chain length and polarity of the substituents and the regularity of their arrangement along the

polymer chain make it possible to control the structural, physicochemical and electrophysical characteristics of polythiophenes in organised planar systems. This primarily corresponds to the control of the effective conjugation length of the polythiophene main chain and to the synthesis of uniformly oriented chains separated by distances which provide charge transfer between the adjacent macromolecules. In certain cases, creation of mixed monolayers of polythiophenes with surfactants (fatty acids, alcohols, amines, *etc.*) increases the stability of monolayers, ensures their transfer onto solid substrates and formation of high-quality multilayer LB films. In these cases, the conducting characteristics of polythiophene films are not inferior to those of similar systems containing pure polythiophenes. The use of dopants allows one to reach the electrical conductivity of substituted polythiophenes in the range from 500 to 1000 S cm^{−1}. The practically important properties of polythiophenes also include the photo- and electrochromic properties as well as the ability to form complexes with metals and gases. These properties enable the use of polythiophenes for creating thin-film light-emitting devices, sensors, *etc.* The Langmuir–Blodgett method has good prospects in this respect as it provides organised ultra-thin films with larger conjugation lengths than those of the films formed from solutions, and hence higher functional capabilities of molecular devices.

Based on the analysis carried out above, we can suggest the directions and priorities in the study of these systems. First, it is necessary to synthesise novel polythiophenes with functional substituents which are regularly distributed along the chain but are not included in each thiophene unit. These substituents can be represented, for example, by azo compounds which can undergo photoisomerisation disturbing the macromolecule conformation, which, in turn, should switch the conjugation length and hence change the conductivity and the chromatic characteristics of the systems. Second, more detailed studies of the structure of monolayers on the surface of water with the use of such methods as optical spectroscopy, Brewster angle microscopy and synchrotron X-ray reflectometry should be carried out. Third, the problem of monolayer stability requires a detailed study. In this connection, studies of the relaxation properties of two-dimensional systems would be rather useful. Fourth, it is necessary to study more intensely the structures of LB films comprising both individual and mixed monolayers. In the latter case, it would be desirable to obtain a consistent model of the distribution of film components in the layers. And, fifth, much greater attention should be given to the development of molecular devices based on LB films consisting of polythiophenes.

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Application of radical cage reactions in studies of microstructures of polymers and composites[†]

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Abstract. The potentialities of radical cage reactions as a tool for investigating the chemical structures of polymers are considered. The kinetic regularities of triplet carbene reactions in the matrix-isolated state and in clusters are analysed to reveal structural features of the cage surroundings. The possibility of determination of structural characteristics of filled polymers from kinetic data is discussed. The bibliography includes 103 references.

I. Introduction

The first ideas about the relationship between chemical kinetics and molecular organisation of media were formulated by academician N M Emanuel back in the 1960s. In particular, he initiated studies on the influence of the physical structure of polymeric systems on the kinetics and mechanisms of reactions which occur in them. These studies were aimed, on the one hand, at creating a theory of processes of polymer ageing¹ and, on the other hand, at the development of scientifically substantiated methods for their stabilisation and prediction of their lifetime under different operation conditions.² Numerous studies carried out in this direction have shown that kinetic regularities of the reactions occurring in solid polymers are functions of their physical-structural properties. In particular, the kinetics of such reactions is associated with the kinetics of molecular motions of macromolecules. Simple kinetic laws were found to be as a rule inapplicable for the description of chemical processes occurring in solid polymers at temperatures below $\frac{2}{3}$ the glass transition.^{3–5}

The formal kinetic regularities of a chemical process in a condensed medium depend on the rapidity of changes in local medium properties, which influence the reactivity of the species involved, *i.e.*, on the relationship of three temporal parameters, *viz.*, the characteristic time of a chemical transformation (τ_{ch}), the lifetime (τ_1) of the process-controlling active centre and the correlation time (τ_c), which is sufficient for all the reactive species present in a given medium to pass through all possible states where they have different reactivities.⁶ If the condensed medium is represented by solid polymers, the correlation time is much longer

than the reaction time ($\tau_c \gg \tau_{\text{ch}}$), *i.e.*, dispersion of species as regards their reactivities is observed (such species are kinetically non-equivalent).⁶ The observed process rate depends on the distribution pattern of the reacting species and its variation with time. In this context, the kinetics of even an elementary reaction in solid polymers is determined by a set of rate constants which characterise the reactivity of a species in a particular surrounding. The effect of local structural-physical properties of solid polymers on the kinetics of reactions occurring in them is the reason for the structural ‘memory’ of the reacting species on their initial distribution as a function of reactivity. Therefore, the kinetics of chemical reactions in polymers depend on the sample prehistory.⁷

Despite the complexity of the analysis of experimental results, kinetic studies of the reactions occurring in solid polymers are of a tremendous theoretical and applied interest. These offer a unique opportunity for elucidating peculiarities of the microstructures of these subjects, since the reaction kinetics is dependent on the initial polymer state and on changes in the distribution of reacting species over local structural parameters. The present review considers the validity of the approach to the estimation of structural-physical and molecular-dynamic characteristics of solid polymers based on the kinetic analysis of a series of pseudoelementary radical cage reactions, in particular, low-temperature decay of triplet carbenes, thermal dissociation of dimers of stable radicals as well as dissociation of macroradicals induced by nitrogen dioxide and salts of transition metals.

II. The choice of model reactions for the investigation of structural-physical properties of polymers

Certain difficulties are related to the choice of versatile model cage reactions, the kinetics of which may be purposefully used for structural studies of polymers. Apparently, this objective can be hardly achieved using complex free-radical processes, such as thermo- and photooxidation including migration of free valence, decay of macroradicals and reactions of oxidation products. The point is that it is difficult to isolate the stages sensitive to definite structural-physical properties of the matrix in these multistage

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[†]Dedicated to the blessed memory of academician N M Emanuel (1915–1984).

[‡]As the temperature increases (above T_g) the intensity of molecular motions is enhanced and the ‘solid-phase’ formal kinetics approaches the conventional liquid-phase kinetics.

processes on the basis of measured kinetic parameters. Even the simpler reaction of thermal decay of radicals cannot always be used as a model. Thus, the death of macroradicals generated by low-temperature photolysis, radiolysis or mechanical impacts on polymers cannot be regarded as the versatile model suitable for the estimation of structural-physical properties, because in this case the mechanism of macroradical decay is rather complicated and may be accompanied by migration of the free valence over considerable distances as the result of diffusion and chemical relay-race. Numerous studies established a characteristic feature of this reaction in solid polymers, *viz.*, its kinetic arrest at constant temperature or its 'stepwise' character.^{6,8} The nature of this phenomenon was rationalised from different stands taking into account the structural-physical heterogeneity of the matrix,^{9,10} differences in the interradsical distances,¹¹ increased concentration of radicals in structural defects,¹² *etc.* However, the kinetic regularities observed in this process can be regarded only as an indirect indication to the dependence of the reactivity-based distribution of radicals on the structural-physical properties of polymers.

Direct analysis of the relationship between kinetic parameters and structural features of the nearest cage environments is confined to those reactions which are not complicated by migration of active centres over considerable distances. These types of processes include, for example, thermal decay of radical pairs (RP) in a cage. In most cases, RP are formed in low-temperature photolysis and γ -radiolysis of frozen solutions or polymers.¹³ The radical pairs arising in radiolysis are sufficiently stable at the temperature of their generation, and processes of their recombination, disproportionation and their exit from the cage can be investigated in the thermal annealing of samples.

Kinetic studies of the RP formation during photodisintegration of a number of low-molecular-weight additives can be used, *e.g.*, for the establishment of the mechanism of radical initiation in the solid phase. The radical pairs offer a unique opportunity for studying structural-physical properties of the medium. The interradsical distances in such pairs can be measured directly by EPR spectroscopy. Thus it was established from the EPR spectra¹⁴ that the mean distance between radicals in the RP generated in the photolysis of a solution of 3,6-di-*tert*-butyl-*o*-benzoquinone and diphenylamine in chlorobenzene changes from 0.62 to 0.64 nm (the accuracy of measurements was 0.005 nm) in the course of RP accumulation, which may be indicative of different geometry of molecular complexes from which these RP were formed.¹⁵ The radical pairs formed under the action of light in monocrystalline matrices in the course of redox reactions involving molecular complexes of quinonediazides with catechols^{16,17} also proved to be kinetically non-equivalent, as followed from the scatter of the rates of their decay during annealing. The solid-phase transfer of hydrogen atoms accompanied by the formation of RP stable at room temperature has been detected in quinone-catechol polycrystalline mixtures under the action of elastic wave pulses.¹⁸⁻²¹ It was shown that in these systems the polymeric matrix decreases the threshold of the elastic wave strength required for the formation of paramagnetic products and enhances the RP stability. It was established²² that the dispersion with respect to the interradsical distances in RP is proportional to the difference between the maximum and minimum activation energies of their decay.

The kinetic non-equivalence of RP may be determined not only by the differences in the interradsical distances, but also by the structural distinctions of the nearest surroundings.^{23,24} Thus the kinetics of thermal dissociation of RP in oriented polyethylene is described by several rate constants, though the mean distance between the radicals ($r_m = 0.53$ nm) remains constant throughout the process. The formation of four types of RP was established in the low-temperature photolysis of single crystals of tetraphenylhydrazine.²⁵ Their formation results from disintegration of molecules differently oriented in a magnetic field. All the four types

are characterised by identical magnetic properties but different rate constants of their decay.

The kinetics of transformation of the RP generated upon γ -irradiation of dimethylglyoxime and dimethylglyoxime- d_2 had been used for the determination of the constants of their decay, the kinetic isotope effect (KIE), the direction of the free valence migration and the distance of the hydrogen atom transfer.²⁶⁻²⁸ Characteristic features of the free valence migration are its stereospecificity, anisotropy of the valence migration directions and sensitivity to weak molecular interactions.

The process of RP recombination does not require relocations of radicals to considerable distances but is rather sensitive to local molecular motions.²⁹ This allows the use of RP reactions for studies of structural transitions and characteristic frequencies of small-scale molecular mobility in a polymeric matrix. Thus in the temperature range from 160 to 260 K, the curves of RP defrosting in polyethylene revealed two structural transitions in the crystalline regions of the matrix. Structural and phase transitions can also be registered from the mean distance between radicals in RP over a wide temperature range.¹³ Kinetic measurements of the exit of radicals from the cage allow determination of the frequency of translational motions.^{23,30}

In principle, the abstraction of a hydrogen atom from the molecules of the medium by active radicals with the formation of a radical matrix can be used as a model of cage reactions.^{25,30} Taking into account that the distance of hydrogen atom transfer is ~ 0.3 nm, one can presume that the kinetic features of this reaction should reflect directly the structural effect of the nearest cage surroundings. However, examples of kinetic studies of the RP reactions and hydrogen abstraction by radicals are mainly confined to the investigations of frozen solutions of low-molecular-weight compounds as well as of mono- and polycrystalline substances (see, *e.g.*, Refs 31-33).

The effect of structural peculiarities of a polymeric matrix at the level of reaction cages on the kinetics of the reactions occurring in the matrix can be studied using the approach proposed by Denisov *et al.*³⁴⁻³⁷ where the reaction of spatially hindered phenoxyl radicals with the hydroperoxide groups of macromolecules has been used for the development of a model of cage reactions



Reaction (1) is the rate-limiting one. This reaction is slow and is not limited by the diffusion of reagents in the case of regular distribution of radicals in the matrix. The phenoxyl radical and the hydroperoxide group enter the reaction cage and react only when they possess sufficient energy E and have a favourable mutual configurations. However, the walls of the cage prevent the achievement of such configuration, and the more 'rigid' the walls the higher the activation energy of the elementary reaction (1). To study the kinetics of this reaction, a stable nitroxyl radical as a spin probe was added along with a phenoxyl radical to the polymer. In this case, the rate constant of the reaction (1) correlated linearly with the frequency of the spin probe rotation (ν_r). Thus the activation energies of the nitroxyl radical rotation in polyethylene, polypropylene and chlorobenzene measured using the EPR spectra at 290-370 K were 28, 32 and 12 kJ mol⁻¹, respectively. The difference in the activation energies of the nitroxyl radical rotation in polymers and chlorobenzene virtually coincided with those for the reaction (1) in the polymer and chlorobenzene.

The results obtained permitted expression of the rate constant of the cage bimolecular reaction (1) in the form

$$k = \frac{6\nu}{n} K_{AB} P_r P \exp\left(-\frac{E_r + E}{RT}\right), \quad (3)$$

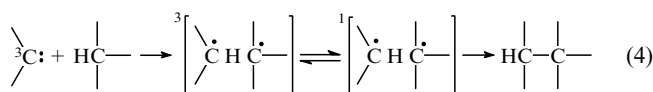
where ν and n are the frequency of collisions and the number of 'neighbours' in the cage, K_{AB} is the equilibrium constant of the

A + B pair formation in the cage, $P_r \exp(-E_r/RT)$ is the probability of rotation of the reagents in the cage resulting in the activated complex configuration and P is the steric factor of the reaction in the liquid phase.³⁶ Thus, the rotation frequency of the reagents in the cage and the frequency-related reaction rate constant characterise the cage surrounding of reagents in polymers.

Of special interest for studies of the microstructures of polymeric objects are versatile cage reactions which can be initiated in various matrices over a wide temperature range. In this connection, many possibilities are provided, *e.g.*, by radical processes such as low-temperature decay of triplet carbenes, macroradical dissociation reactions induced by nitrogen dioxide and photoreduction of transition metal salts and thermal dissociation of dimers of stable radicals.

III. Assessment of the structural-physical heterogeneity of polymers from the kinetics of thermal decay of carbenes

Carbenes are most often generated in thermal, thermocatalytic and photochemical degradation of diazo compounds.³⁸ The reactivities of the carbenes formed depend on their spin states.^{39, 40} Insertion into ordinary chemical bonds in a one-step mechanism and also stereospecific addition to double bonds with formation of cyclopropanes are typical reactions of carbenes in a singlet state. The triplet carbenes are also characterised by insertion reactions but these are multistep reactions. Let us consider the reaction of low-temperature decay of triplet carbenes in solid polymeric matrices.



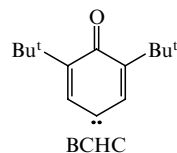
In the first step, the transfer of hydrogen atom[§] from the surrounding macromolecules to a matrix-isolated triplet carbene results in the formation of a short-lived RP in the triplet state which then undergoes triplet–singlet conversion. The RP in the singlet state resulting from this conversion can recombine with formation of the final product of carbene insertion into the C–H bond of the macromolecule. The dynamics of H atom transfer and RP recombination in polymers depends on the polymer structure.

The frequency of the triplet–singlet transition in RP is $\sim 10^8 \text{ s}^{-1}$ (Ref. 41). It is known that the frequency of small-scale molecular motions associated with rotational oscillations of the side groups of macromolecules is of the same order.⁴² Thus, the spin evolution of RP generated in reaction (4) is within the same time scale as the molecular dynamics, which determines dislocations and rotations of the side groups of macromolecules in the cage.

Numerous studies have shown that if the ground state of carbenes is triplet, then the efficiency of carbene transformations by the ‘abstraction–recombination’ mechanism (4) in the transition from the liquid to the solid phase with a decrease in temperature is drastically increased.^{38, 43, 44} The effective constants of the decay rate of triplet carbenes determined experimentally at cryogenic temperatures are very small. For example, they amount to $10^{-3} - 10^{-4} \text{ s}^{-1}$ for different frozen organic matrices (Ref. 45).

One should note the principal distinction of the short-lived RP, appearing as active intermediates in the process of triplet carbene decay from the RP which can be registered owing to the characteristic EPR spectra in frozen solutions of low-molecular-

weight compounds and polymers.¹³ The former type includes the short-lived species whose lifetime in the cage is comparable with the time of their spin conversion ($\sim 10^{-8} \text{ s}^{-1}$). They cannot be recorded by the usual EPR method. However, the existence of such species is confirmed by the influence of the magnetic field on the decay rate of the triplet di-*tert*-butylcyclohexadienone carbene (BCHC) (at 77 K) in hexaethyldisiloxane, ethyl acetate, poly(methyl methacrylate) (PMMA) and cellulose triacetate (CTA).^{46, 47}



The high decay rate of the intermediate RP formed in this process is determined by a small interrational distance ($\sim 0.3 \text{ nm}$) and retardation of rehybridisation of chemical bonds⁴⁸ in the radicals of the ion pair due to difficulties in structural relaxation. As a result of relaxation processes, such pairs can be transformed into RP of the second type ($r > 0.3 \text{ nm}$) which are comparable with free radicals in their thermal stabilities.

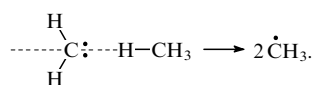
1. The effect of spatial orientation factors on the decay kinetics of carbenes in polymers

A characteristic feature of cage reaction (4) of low-temperature decay of carbenes in solid polymers is the kinetic non-equivalence of species.⁴⁹ The time dependence of carbene concentration (N) is described by the following expression:

$$N(t) = N_0 \int_{k_{\min}}^{k_{\max}} \rho(k) \exp(-kt) dk, \quad (5)$$

where $\rho(k)$ is the distribution function of carbenes over decay rate constants. It is natural to presume that the reactivities of carbenes depend on local orientations of the carbene centre and the C–H bonds of the macromolecular matrix in the cage, with a definite decay rate constant corresponding to each orientation. In the system of reaction cages, the distribution $\rho(k)$ changes with the gradual disappearance of carbenes which are best suited for the H atom transfer onto them. Because there is strong restraint of molecular motions in the solid matrix at low temperatures, the favourable orientations of carbenes are not recovered. This structural effect was illustrated by the dependence of the initial decay rate of diphenylcarbenes (DPC) in propanol at 77 K on the duration of their photoregeneration from diphenyldiazomethane (DDM).^{50, 51}

The results reported by Bauschlicher *et al.*⁵² can be used for the theoretical substantiation of the decisive effect of carbene distribution over spatially oriented parameters on their kinetic non-equivalence in the insertion into the C–H bonds of the solid matrix. These authors calculated the ideal geometric configuration of the classical transition state, which corresponds to the minimum height of the potential barrier of the reaction of triplet methylene with a hydrogen molecule and methane. It was shown that hydrogen atom transfer over the trajectory lying in the methylene plane and passing along the bisecting line of the H–C–H angle corresponds to this configuration:



In this case the calculated height of the potential barrier was 103 kJ mol^{-1} . Upon changes in the geometric configuration of the transition state, *i.e.*, the deviation of the trajectory of the migrating hydrogen atom from the ideal one by $20-40^\circ$, the height of the potential barrier increased to 110 kJ mol^{-1} .

The decay kinetics of cyclohexadienone carbenes (CHC) in PMMA at 77–160 K is well described by the equation⁵³

§ The transfer of an H atom requires the approaching of carbene and C–H bond of the macromolecule to a distance of 0.3–0.4 nm and it is these distances that are realised in the cage.

$$N(t) = N_0 \exp(-at^{1/2}), \quad (6)$$

where a is the temperature-dependent parameter. This equation also describes the decay of other carbenes in the glassy and polycrystalline matrices of low-molecular-weight compounds.^{51,54,55} Kinetic equation (6) is derived from Eqn (5) where the distribution function $\rho(k)$ is expressed as:^{56,57}

$$\rho(k) = \frac{a}{k^{3/2}} \exp\left(-\frac{a^2}{4k}\right). \quad (7)$$

The distribution function (7) has a maximum at $k = a^2/6 = k'$. The latter value is the most probable magnitude of the rate constant. Thus, the observed kinetic regularities of the CHC decay in PMMA are explained by the distribution of decay rate constants over the species.

A different kinetic law was established for the decay of BCHC in PMMA.⁵⁸ In this case, the kinetic curves are linearised in the coordinates N/N_0 vs. $\ln t$. It is this kinetic description that is characteristic of the processes with a kinetic arrest, for which the function of distribution over rate constants has usually the form⁵⁹

$$\rho(k) = \frac{1}{k \ln(k_{\max}/k_{\min})}, \quad (8)$$

where $k_{\max}$ and $k_{\min}$ are the boundary values of rate constants. Function (8) corresponds to a rather wide distribution of carbenes with respect to their reactivities, while the kinetic dependence satisfying this distribution is expressed as

$$N(t) = N_0 \left[-\frac{\ln(k_{\min}t)}{\ln(k_{\max}/k_{\min})} \right]. \quad (9)$$

Yakimchenko and Degtyarev⁵⁷ noted that the distribution function (7) is approximated by function (8) for the values of $k > k'$, i.e., where the distribution of species over rate constants is rather narrow: $\ln(k_{\max}/k_{\min}) < 10$. In this case, the k' value correlates with $k_{\min}$, whereas the $k_{\max}$ value may be determined from the initial decay rate of carbenes.

The effect of the spatial orientation factor on the kinetic non-equivalence of carbenes results directly from comparison of the reactivities of CHC and BCHC. Thus at 77 K, the width of distribution regarding the rate constants of CHC decay $\ln(k_{\max}/k_{\min})$ is equal to 5, whereas the same parameter for BCHC is 13. Apparently, introduction of bulky *tert*-butyl substituents into the carbene structure increases the set of the carbene centre orientations relative to the C–H bonds of the surrounding macromolecules and largely expands the distribution of carbenes regarding their reactivities.

The temperature dependences of the rate constants of the H atom transfer to carbenes in polymers (e.g., upon decay of DPC in PMMA) confirm the decisive effect of spatial orientations in the cages on the kinetic non-equivalence of carbene species, which is evidenced by an obvious deviation of these dependences (Fig. 1, lines 1 and 2) from the Arrhenius law (dashed lines in Fig. 1). The effective activation energies decrease with a decrease in temperature from 12–16 kJ mol⁻¹ to an abnormally low value of ~ 5 kJ mol⁻¹ (see Refs 49, 53, 58, 60–62).

The qualitatively similar temperature dependences were also observed for the cage reaction of hydrogen atom abstraction from the solid matrix molecules by free radicals following the tunnelling mechanism.^{31,63} This mechanism takes into account the intermolecular oscillations resulting in changes in the height and width of the potential barrier of the process.^{31,64,65} The temperature dependences of rate constants in both processes can be expressed by the exponential law

$$k(T) = \alpha \exp(\beta T), \quad (10)$$

where α and β are the parameters characterising the properties of the species and the matrix.

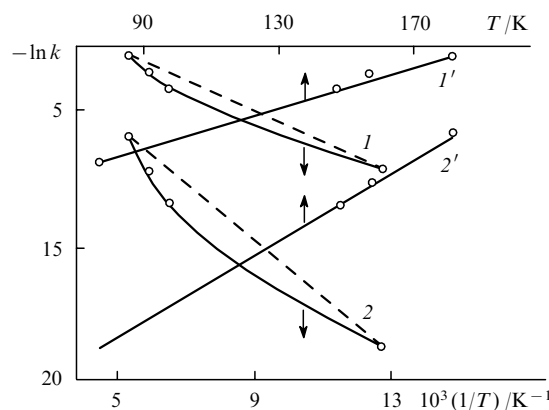
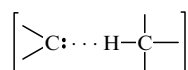


Figure 1. Temperature dependences of the rate constants of DPC decay in PMMA $k_{\max}$ (1, 1') and $k_{\min}$ (2, 2');⁶⁰ (1) and (2) dependences of the form $-\ln k \sim T$; (1') and (2') dependences of the form $-\ln k \sim (1/T)$.

It should be noted that the dependence (10) is well described by the tunnelling mechanism of H atom transfer for the entire series of carbenes, as indicated by the similarity of temperature dependences for $k_{\max}$ and $k_{\min}$. The corresponding representations of $k_{\max}$ and $k_{\min}$ in the reaction of DPC decay in PMMA are presented in Fig. 1 (curves 1' and 2'). These results show that the kinetic non-equivalence of carbenes in polymers is due to the same reason, viz., the scatter of parameters (the width and height of the potential barrier) of the tunnelling transfer of the hydrogen atom. The width of carbene distribution with respect to these parameters is in turn determined by geometric heterogeneities of the reaction cages.

According to the tunnelling model of H atom transfer, a bond of the hydrogen-bond type is formed between the C–H bond of the matrix molecule and carbene.



Molecular oscillations in this complex result in changes in the permeability of the potential barrier to H atom transfer. The higher the temperature the larger the amplitude of intermolecular oscillations and the closer the reagents can come to each other and, consequently, the more probable is the tunnelling process. Thus, the effective potential barrier decreases as the temperature increases, and the rate of the process increases accordingly. Vorotnikov *et al.*^{61,66,67} determined the values of parameters for the tunnelling of H atom to CHC and DPC in the same polypiperylene matrix. The height U and the width x of the potential barrier as well as the equilibrium distance (R_0) between carbon atoms of the active centre of carbene and the C–H groups of polypiperylene in the carbene–polypiperylene complex were determined from the kinetic data obtained at 77–133 K. The boundary values of these parameters, which correspond to the maximum and minimum rate constants of carbene decay, are presented in Table 1. These results indicate that the width and height of the potential barrier decrease with the increase in temperature. These values are somewhat higher for DPC than for CHC, which is indicative of the higher CHC activity in the reaction of H atom abstraction in the same polymeric matrix.

Also worthy of note is the proximity of parameters of the hydrogen atom tunnelling from macromolecules to triplet carbenes and the corresponding values of parameters of the H atom tunnelling to macroradicals in their low-temperature decay by the relay-race mechanism.⁶⁵

The frequencies of intermolecular oscillations in a polymer which activate the H atom transfer were estimated from the KIE determined for the low-temperature decay of BCHC and DPC in common and perdeuterated PMMA and polystyrene (PS). The

Table 1. Parameters of the hydrogen atom tunnelling from the polypiperylene molecules to CHC and DPC.⁶⁷

Carbene	T/K	$U_{\min}^a$	$U_{\max}^a$	$x_{\min}$ /nm	$x_{\max}$ /nm	$R_0^{\min}$ /nm	$R_0^{\max}$ /nm
CHC	~ 0	150	208	0.115	0.140	0.375	0.400
	77	125	150	0.100	0.115	0.375	0.400
	133	108	121	0.094	0.100	0.375	0.400
DPC	~ 0	167	188	0.120	0.130	0.360	0.370
	77	138	159	0.110	0.118	0.360	0.370
	133	121	138	0.103	0.110	0.360	0.370

^a In kJ mol⁻¹.

KIE was shown to be dependent on the reactivities of carbenes. Ensembles of carbenes characterised by higher decay rate constants manifest lower KIE at a given temperature. At $T > 100$ – 115 K, the kinetic isotope effect virtually disappears. The regularities observed are explained in terms of the model of H atom tunnelling across a potential barrier which oscillates due to intermolecular vibrations.

It was shown that for a temperature increase in the range

$$\frac{\hbar\Omega}{4k} < T < \frac{\hbar M\Omega^2}{m\omega_{\text{C}} + \hbar k}$$

[Ω is the characteristic frequency of intermolecular vibrations in the complex, M is the normalised mass of the carbene-CH (or CD) group complex] the KIE should decrease linearly in reactions of hydrogen atom transfer in conformity with the equation

$$\ln \frac{k_{\text{H}}}{k_{\text{D}}} = \left[\frac{\Theta^{1/2} R_0^2 (m_{\text{D}}^{1/2} - m_{\text{H}}^{1/2})}{2\hbar} \right] - \left[\frac{\Theta R_0^2 k T (m_{\text{D}} - m_{\text{H}})}{2\hbar^2 M Q^2} \right], \quad (11)$$

where $\Theta = m_H \omega^2_{C-H} = m_D \omega^2_{C-D}$ is the parameter characterising the rigidity of the C-H and C-D bonds; R_0 is the distance between the potential wells for the H and D atoms. At higher temperatures

$$T > \frac{\hbar M \Omega^2}{m \omega_{\text{C-H}} k}$$

KIE varies in conformity with the T^{-2} law:

$$\ln \frac{k_H}{k_D} \approx \frac{\hbar}{2\Theta^{1/2}} \left(\frac{1}{m_H^{1/2}} - \frac{1}{m_D^{1/2}} \right) \left(\frac{M\Omega^2 R_0}{kT} \right)^2. \quad (12)$$

Analysis of KIE in the reaction of BHC decay in PMMA^{66,67} was performed using relations (11), (12) and the condition $T \approx \hbar m \Omega^2 / m \omega_{C-H} k$, under which the linear temperature dependence is transformed into a T^{-2} dependence. The derived values of characteristic frequencies of intermolecular vibrations ($\Omega \approx 53 \text{ cm}^{-1} \approx 10^{13} \text{ s}^{-1}$) correlate with the Debye frequencies for molecular crystals.⁶⁸ The difference of distances ΔR_0 between potential wells in the reaction of H(D) transfer in different kinetic ensembles of carbenes was also determined from the temperature dependence of KIE.^{48, 66, 69} It turned out that the decrease in the rate constant of BHC decay by one order of magnitude corresponds to $\Delta R_0 \approx 0.006 \text{ nm}$. Such a drastic rate dependence on the distance between reagents is in agreement with the tunnelling mechanism of H atom transfer to triplet carbenes.

Unique information about the nature of the kinetic non-equivalence of carbenes in solid polymers can be obtained from studies of the magnetic field effect (MFE). Numerous literature data (see, *e.g.*, Refs 70–72) demonstrate the possibility of using this effect for the establishment of a detailed mechanism of

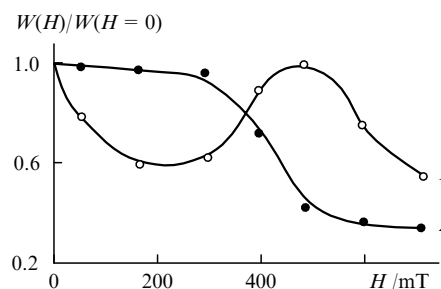


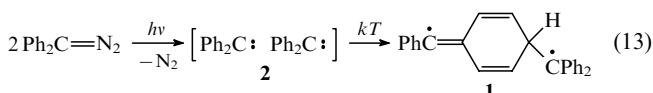
Figure 2. Effect of magnetic field on the rate of BCHC decay in PMMA (1) and CTA (2) at 77 K.⁶⁷

processes involving RP. The application of a magnetic field was shown^{46, 67, 69} to influence noticeably the rate of low-temperature decay of BCHC in PMMA and CTA (Fig. 2); however, the character of this influence is different. Based on experimental dependences $W = f(H)$, the effect of magnetic field is explained by the strong exchange interaction J between unpaired electrons and short-lived RP.⁷¹ From the character of MFE, one can draw a conclusion about the existence in polymers of a set of RP differing in energies of exchange interactions. Poly(methyl methacrylate) is more homogeneous than cellulose triacetate, which is reflected in a smaller set of cages with different exchange energies in the radical pairs. The distribution of RP with respect to J corresponding to the scale of the observed effect is determined by the orientational factor associated with different angles of rotation of the axes of the orbitals of unpaired electrons relative to each other in RP.⁷³

The effect of magnetic field on the decay of carbenes in solid polymers is analogous to its influence on their decay in low-molecular-weight organic glasses; however, the scale of the MFE is different. This provides evidence that the extent of differences in the character of MFE is determined not only by the nature of RP, but also by the nature of the matrix. In low-molecular-weight glasses, the reaction cages are more homogeneous with regard to the structural-physical parameter J compared to polymeric matrices.

2. Determination of molecular-dynamic characteristics of polymers from the transformation kinetics of carbenes in clusters

Diazo compounds, like many low-molecular-weight additives, are irregularly distributed in solid polymers due to the existence of defects in the packing of macromolecules.⁷⁴ This leads to a higher concentration of diazo compounds in the regions with a decreased packing density of macromolecules, which can result in the formation of clusters. Thus EPR spectroscopy revealed that photolysis (at 77 K) of DDM in common and perdeuterated PMMA, PS and polycarbonate (PC) resulted in carbenes $\text{Ph}_2\text{C:}$ formed in the matrix-isolated state and also biradicals **1**^{75, 76} generated in the regions with a decreased packing density of macromolecules due to conversion of DPC dimers (**2**) in clusters according to the scheme



The EPR spectrum of biradicals generated in reaction (13) is shown in Fig. 3*a*. It represents an anisotropic signal with the parameters of cleavage in a zero field $D_{\perp} = 11$ mT and $D_{\parallel} = 22$ mT. The mean distance between unpaired electrons is 0.63 nm. The formation of biradicals in reaction (13) is confirmed by the increase in their yields at higher DDM concentrations. At

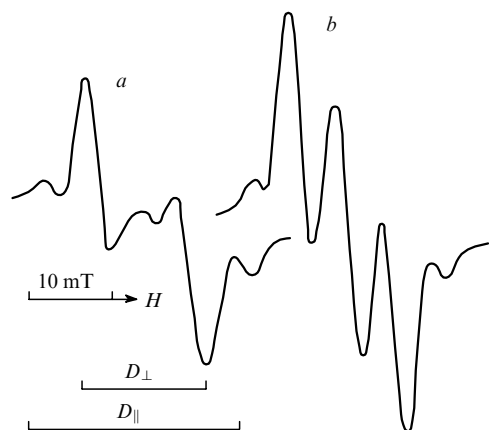
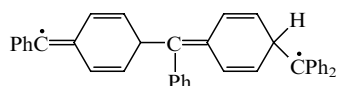


Figure 3. EPR spectra of biradicals generated in the photolysis of polymers supplemented with DDM at 77 K.⁷⁵ [DDM] (mol kg⁻¹): (a) 0.1; (b) 0.2.

sufficiently high [DDM] (~ 0.2 mol kg⁻¹) a signal of biradicals comprising three or more DPC fragments appears in the central part of the EPR spectrum (Fig. 3 b):



Such species arise in bulkier clusters, their proportion in PC and PMMA does not usually exceed 20% of the total quantity of biradicals.

Reactions of carbenes localised in clusters are interesting in two respects: the yield of biradicals **1** reflects the irregularity of the distribution of carbene precursors as regards their concentrations and this can also be used for the estimation of distribution of other low-molecular-weight additives as regards their concentrations in solid polymers. For example, an analogous distribution of bimolecular, trimolecular and larger clusters should apparently be expected for a number of photostabilisers, antioxidants and photosensitisers (salicylates, bisphenols, benzophenones).

In addition, the kinetics of biradical formation may be used to characterise the intensity of molecular mobility of the cluster surrounding. The kinetics of biradical generation in clusters at 77–120 K is well described by the logarithmic dependence on time. Analysis of experimental kinetic dependences performed by Davydov *et al.*^{66,75} made it possible to establish the distribution pattern of rate constants as regards the Arrhenius parameters. In general case, the reactivities of carbenes in clusters can be determined from the distribution with respect to both effective activation energies of reaction (13) and preexponents.⁷⁷

Figure 4 shows the integral distribution functions $\Theta(E)$ and $\Theta(k_0)$ for the formation of biradicals involving DPC in polycarbonate. As the dependences shown in Fig. 4 are virtually linear, the functions of carbene distribution in clusters with respect to the Arrhenius parameters may be regarded as 'rectangular':

$$\frac{d\Theta(E)}{dE} = \frac{1}{(E_{\max} - E_{\min})}, \quad E_{\min} \leq E \leq E_{\max};$$

$$\frac{d\Theta(k_0)}{d \log k_0} = \log \left(\frac{k_0^{\max}}{k_0^{\min}} \right), \quad \log k_0^{\min} \leq \log k_0 \leq \log k_0^{\max}.$$

The limit values of the Arrhenius parameters in PC are as follows: $E_{\max} = 38$ kJ mol⁻¹, $E_{\min} = 26$ kJ mol⁻¹, $\log k_0^{\max} = 14.4$, $\log k_0^{\min} = 12.8$. The values of the activation energy are typical of the relaxation processes in RP determined by motions of monomer units of macromolecules. These values are in good

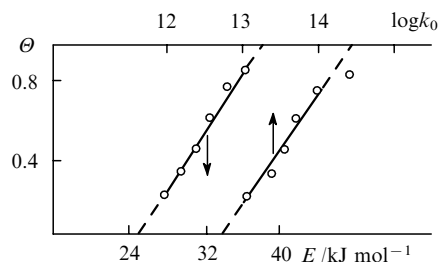


Figure 4. Integral functions of DPC distribution with respect to the Arrhenius parameters of biradical generation in PC.⁷⁵

agreement with the activation energies of the spin probe rotation.^{78,79} Thus, it may be concluded that the rate of reaction (13) in PC is controlled by the vibrational mobility of carbenes in clusters. Indeed, the values of $k_0 = 10^{13} - 10^{14}$ s⁻¹ are comparable with the frequencies of motions of low-molecular-weight species in polymers. One should note a relatively narrow dispersion of the Arrhenius parameters in PC: $\Delta E = 12$ kJ mol⁻¹, $\log k_0 = 1.6$.

In PMMA, the limiting values of the Arrhenius parameters are as follows: $E_{\max} = 50$ kJ mol⁻¹, $E_{\min} = 22$ kJ mol⁻¹, $\log k_0^{\max} = 16.0$, $\log k_0^{\min} = 10.5$ kJ mol⁻¹. The mean values of these parameters ($E_{\text{mean}} = 36$ kJ mol⁻¹, $\log k_0^{\text{mean}} = 13.25$) correlate with the activation energy of rotation and the correlation time of the spin probe in PMMA ($E = 38 - 42$ kJ mol⁻¹, $\log \tau = 13.2$).⁷⁸ Of definite interest is a rather broad dispersion of parameters ($\Delta E = 28$ kJ mol⁻¹, $\Delta \log k_0 = 5.5$), which seems to be due to a large set of molecular motions in PMMA at given temperatures. Indeed, the relevant calculations⁸⁰ show that the activation energy of rotational motions in the ester groups of PMMA with concomitant vibrations of the main chain segments near the equilibrium positions is 21.6 kJ mol⁻¹. This value correlates with the minimum activation energy of biradical formation. The activation barrier to rotation of the ester groups increases with the deviation of rotation angles of the main chain segments from their equilibrium values. Relevant calculations give a maximum potential barrier of 68 kJ mol⁻¹ for the torque vibrations about the C–C bonds of the main chain.⁸⁰ Therefore, the increase in the activation energy of reaction (13) to 50 kJ mol⁻¹ is indicative of the existence of ensembles whose reactivities are controlled by the mobilities of segments of the main macromolecular chain.

The results obtained^{75,76} make it possible to consider the reaction of biradical formation in DPC clusters as a specific probe for studying the molecular dynamics of macromolecules at low temperatures. The conventional method based on the use of a paramagnetic probe⁷⁹ is little suited for studies of molecular mobility in polymers at temperatures below the glass transition point. For $T < T_g$, EPR spectroscopy makes it possible to record only a part of the high-frequency spectrum of vibratory motions of the probe. The method based on measurement of the kinetics of DPC transformation in clusters extends considerably the temperature range for studies of the small-scale dynamics of macromolecules. This allows determination of molecular-dynamic characteristics of polymers in the temperature range 90–220 K where the use of other methods is problematic.

IV. Estimation of structural characteristics of filled polymers from the kinetics of cage reactions

Structural-physical modification of polymers at the macroscopic level has a strong effect on the reactivities of radicals in the cage. One of the most popular methods for the modification of the physical structure of polymers is to fill them with inorganic additives. Numerous studies have shown that the effect of polymer filling is associated with the formation of boundary layers^{81–85} with structures noticeably different from the bulk structure of

polymeric medium. The effective width of the boundary layer measured experimentally was found to reflect the behaviour of the filled system in respect of the property under study, *i.e.*, this characteristic can be changed depending on the technique used for its measurement. Information about the boundary layers is as a rule derived from physicochemical parameters which are essentially dependent on the degree of filling, *e.g.*, from the heat capacity (in the range of glass transition temperatures),⁸⁶ density⁸³ and viscosity.⁸⁷ Due to a close relationship between the structural-physical properties of polymers and the kinetics of reactions occurring in them, investigation of kinetic dependences may also be regarded as an informative method for the determination of structural characteristics of filled polymers, in particular of the effective thickness of the boundary layers.

There is a large body of literature data devoted to the analysis of regularities of the thermal decay and thermal oxidation of filled polymers (see Bryk's monograph⁸⁸ and references cited therein). The available information points to a substantial role played by the filler in these processes. However, at high temperatures the kinetics can be influenced, in addition to the structural-physical factor, by the catalytic properties of the filler surface. From this viewpoint, the use of cage radical reactions occurring at low and moderate temperatures offers definite advantages for the estimation of the effect of the structural factor. The kinetics of these reactions should reflect peculiarities of the molecular organisation of boundary layers and the reactions must not be complicated by the interaction of radicals with the filler surface.

1. Effect of the filler on the kinetics of low-temperature decay of matrix-isolated carbenes

Filling of PMMA and TFC with Aerosil decreases the rate of low-temperature decay of BCHC in these polymers.^{66, 89} This effect was observed at 100–140 K. The increase in the filler content decreases the limiting rate constants $k_{\max}$ and $k_{\min}$; however, the width of the distribution as regards the rate constants $\log(k_{\max}/k_{\min})$ remains invariable and amounts to 6.8 in PMMA and 5.5 in CTA at 100 K. As the temperature increases, the constancy of the distribution with respect to the reaction rate constants under isothermal conditions is also confirmed by the approximation of the stepped kinetic curves to the equation

$$\frac{N}{N_0} = (1 + nk_0t)^{-1/n},$$

where n is the parameter characterising the distribution width of carbenes as a function of their reactivities and k_0 is the mean effective rate constant.⁹⁰ Despite different contents of Aerosil, the kinetics of low-temperature BCHC decay in PMMA and CTA is characterised by the parameter n which is constant at a given temperature.^{69, 89}

Figure 5 shows the dependence of k_0 on the distance l between the filler particles. One can see from the graphs presented in Fig. 5 that k_0 varies little at $l > 20$ nm, though it decreases by more than one order of magnitude at $l < 20$ nm. Such a drastic drop of the process rate is related to changes in the physical structure of the polymeric matrix upon transition to the state of boundary layers. The structural rearrangement changes the ratio of the rates of individual stages of BCHC decay as well as the relative population density of the triplet and singlet states of the intermediate RP resulting from changes in their configurations and, consequently, in the exchange energies. All these factors lead to a lower k_0 constant. The kinetic data obtained indicate that the effective thickness of the boundary layers of the filler in PMMA and CTA ranges from 15 to 20 nm.

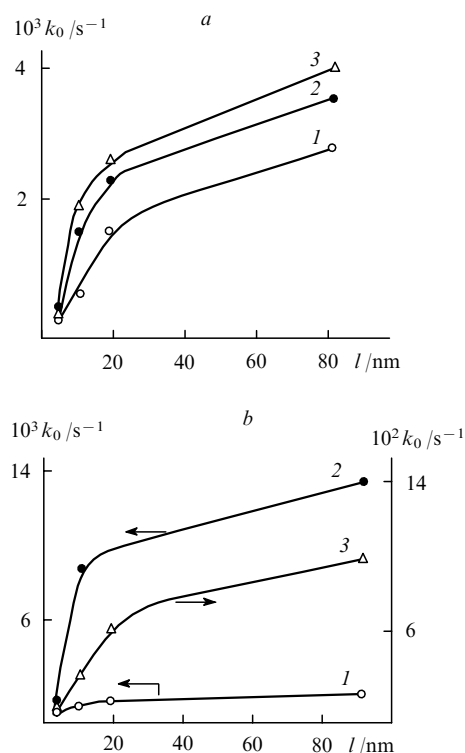


Figure 5. Dependence of the mean rate constant of BCHC decay on the distance between Aerosil particles in PMMA (a) and CTA (b);⁸⁹ (a) $T = 100$ (1), 113 (2), 125 K (3); (b) $T = 100$ (1), 125 (2), 135 K (3).

2. Effect of the filler on the kinetics of carbene transformation in clusters

In the example of filled PC, the reaction (13) of generation of biradicals in DPC clusters is shown to be noticeably influenced by the presence of a filler.^{75, 76} Figure 6 shows the temperature dependence of the molecular mobility (the 'defrosting' curves), which reflects the reactivity of carbenes and biradicals in DPC clusters, on the Aerosil content in PC. The maximum quantity of biradicals is formed in the Aerosil-free PC at 130–150 K, while the molecular mobility is unfrozen for all ensembles of carbenes. In the filled samples, the maximum is shifted towards lower temperatures ($T \approx 120$ K), because at $T > 120$ K the biradicals

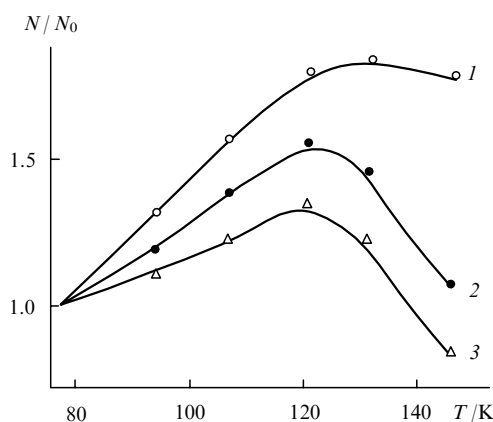


Figure 6. Temperature dependences of the yield of biradicals in the Aerosil-free (1) and Aerosil-filled (2, 3) PC.⁷⁵ The content of the filler (mass %): 50 (2), 65 (3).

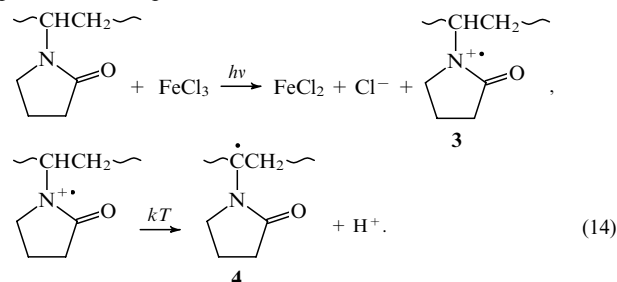
are thermally destroyed in these samples. The different time course of the unfreezing curves is determined by a considerable decrease in the thermostability of biradicals with the increase in the degree of polymer filling. The kinetics of biradical decay in PC at different filler contents may be used for the estimation of the effective thickness of boundary layers.⁷⁵ We give below the initial decay rates of biradicals (BR) in the filled PC at 146 K, relative to their initial concentration depending on the proportion (vol.%) of Aerosil V_a .

V_a (%)	0	22	30	40
$(W_0/[BR]_0) \times 10^4 / s^{-1}$	0.25	3	9	15

The non-additive character of the initial rate dependence on V_a and its dramatic increase at $V_a > 20\%$ are determined by the transition of the polymer to the structural state of the boundary layer. The boundary layer thickness was found to be 12 nm. This magnitude is rather close to the value derived from the filler effect on the decay kinetics of the matrix-isolated carbenes.

3. Effect of the filler on the transformation kinetics of macroradicals

Structural modification of polymers upon their filling is reflected in the kinetics of other elementary reactions, in particular of the monomolecular decay of macroradicals. Thus it was found that the kinetics of the radical decay of polyvinylpyrrolidone (PVP) initiated by photoreduction of Fe(III) additives at 77 K^{49,91,92} is dependent on the presence of a filler.



Degradation of the radical cations **3** in the thermal stage results in the formation of macroradicals **4** which are identified from their EPR spectra. The effect of the Aerosil filler on the efficiency of generation of the radicals **4** is reflected by the unfreezing curves shown in Fig. 7. The maximum relative quantity of the radicals **4** is registered at 180–200 K. This characterises the proportion of their precursors, *viz.*, radical cations **3**, which are stabilised in the low-temperature photolysis of samples. It follows from the plots shown in Fig. 7 that in highly filled PVP only 10% of the radical cations **3** are stabilised at 77 K, whereas their content reaches $\sim 70\%$ in non-filled samples. The non-linear character of variation of the radical concentration at a given

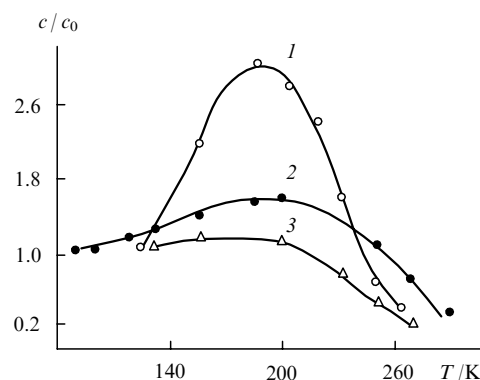
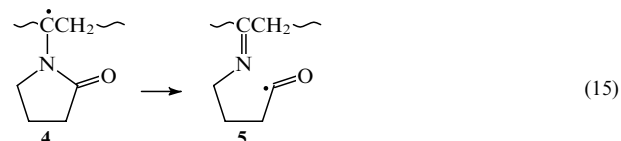


Figure 7. Temperature dependences of the yield of macroradicals **4** in the Aerosil-free (**1**) and Aerosil-filled (**2**, **3**) PVP. The filler content (mass %): 15 (**2**), 50 (**3**).⁹²

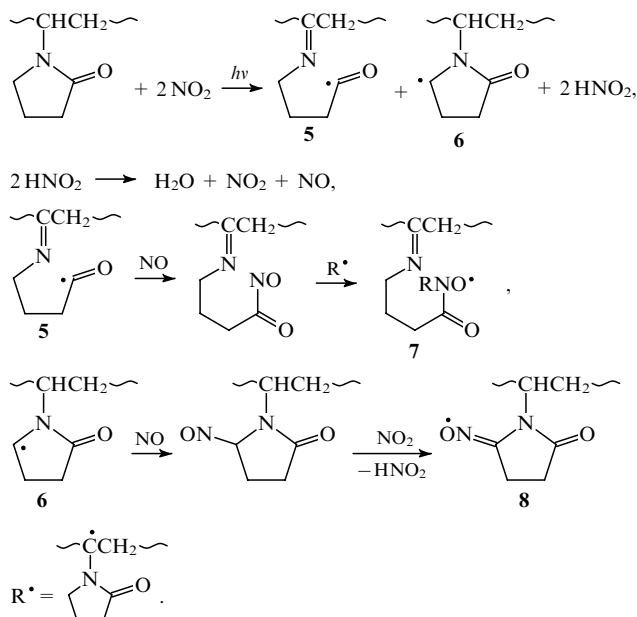
temperature as a function of the filler content is determined by the structural transition occurring in PVP upon addition of definite amount of Aerosil, *i.e.*, upon transition of the polymeric phase to the boundary layer state. The effect of structural modification on the efficiency of transformation of the radical cations **3** in reaction (14) is particularly strong where the amount of the filler is 50 mass%, which makes the distance between the filler particles equal to ~ 25 nm. This distance may be regarded as the effective thickness of the boundary layer. The observed effect seems to be caused by the formation of a looser molecular packing compared to that in the polymer bulk. The decrease in the molecular packing density favours the lowering of the energetic barrier to rehybridisation of the carbon atom⁴⁸ in macroradicals **4** from the sp^3 to the sp^2 configuration in the reaction (14). As a result, the activation energy of reaction (14) is decreased in the case of filled PVP compared to that in the non-filled polymer and the concentration of the radicals **4** increases accordingly in the photoinitiation at 77 K.

The application of the above reactions to the structural studies is limited to rather low temperatures. The expansion of the temperature range requires further search for radical reactions, the kinetics of which reflect the structural effect under conditions of usual and elevated temperatures and can be measured in a fairly simple manner.

From this standpoint, highly interesting are the reactions in which active radicals may be transformed into stable radicals which can be recognised by their characteristic EPR spectra. Thus dissociation of the radicals **4** leads to the pyrrolidone ring opening, which is accompanied by the formation of radicals **5**.



However, because of their low stabilities, radicals **5** could not be registered by EPR spectroscopy. For this reason, the course of reaction (15) was monitored by following the transformation of the radicals **5** into stable nitroxyl radicals under the action of nitrogen dioxide on the initial and Aerosil-filled (50 mass %) PVP.^{93,94} Under these conditions, free-radical transformations of PVP occur according to the following scheme:⁹⁵



These reactions result in the formation of two stable nitroxyl radicals, *viz.*, **7** and **8**. The EPR spectrum recorded after exposure of PVP in NO_2 represents superimposition of the signals from these radicals (Fig. 8a). The content of the radicals **7** is markedly

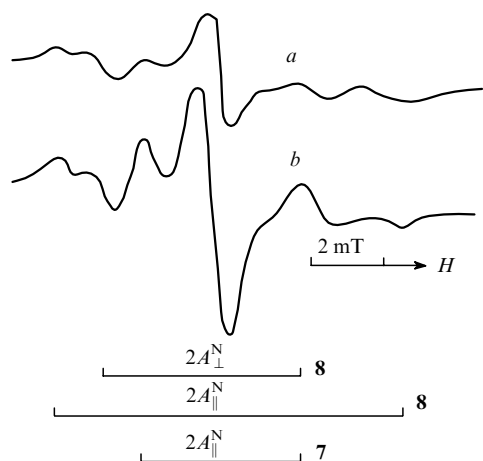
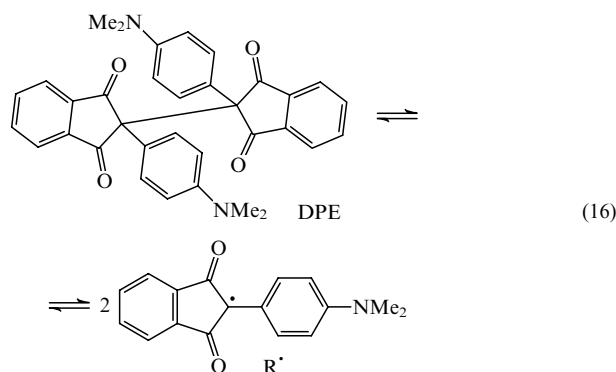


Figure 8. The EPR spectra of polyvinylpyrrolidone after its irradiation in the presence of NO_2 .⁹⁴ (a) Aerosil-free PVP; (b) PVP with 50 mass % of Aerosil.

increased in highly filled PVP (Fig. 8b). This fact points to an increase in the efficiency of formation of their precursors, viz., radicals **5**, in reaction (15) owing to a decreased density of molecular packing upon formation of boundary layers. Thus, the proportion of the signal from the radicals **7** in the overall EPR spectrum may be regarded as an indirect characteristic of the depth of the structural-physical modification of the filled polymer.

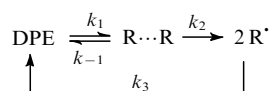
4. Kinetic features of the dissociation of radical dimers in filled polymers

Structural characteristics of filled polymeric compositions can be estimated at relatively high temperatures using the cage reaction of thermal dissociation of diphthaloylthane (DPE) into two stable radicals.^{96–98}



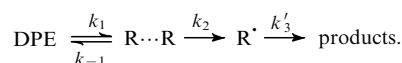
The reaction (16) is an equilibrium one in liquid state. However, kinetic studies of the DPE-free radicals system in CTA at 320–370 K pointed to a more complex mechanism of this reaction in the solid polymer matrix.^{99, 100}

In the temperature range 320–334 K this process follows the scheme



In the first step, dissociation of DPE yields RP. The rigid cage surrounding it prevents the exit of radicals from the cage. Therefore, some radicals recombine in the cage, while those released into the bulk of the system are transformed into initial DPE as a result of diffusive collisions. At higher temperatures (344–364 K), the reaction scheme is different, which is related to the change in the

mechanism of radical decay. In this case, the linear loss of radicals occurs instead of the quadratic loss.



Taking account of the steady-state concentrations of RP and provided $k_{-1} \gg k_2$, the equations for the steady-state concentrations of radicals are expressed as

$$[\text{R}^{\bullet}]_c = \sqrt{\frac{k_1 k_2 [\text{DPE}]_0}{k_{-1} k_3}}, \quad (17)$$

$$[\text{R}^{\bullet}]_c = \frac{k_1 k_2 [\text{DPE}]}{k_{-1} k'_3}. \quad (18)$$

Structural modification of CTA upon its filling with Aerosil (up to 60%) influences the reactivity of the radicals $\text{R}^{\bullet}$. This effect is demonstrated in Fig. 9, which shows the temperature dependences of the steady-state concentration of radicals in the original and Aerosil-filled CTA. At $T > 340$ K, the concentrations of $\text{R}^{\bullet}$ in the filled samples are higher than those in the Aerosil-free samples. However, the reverse temperature dependence is observed in the high-temperature range. The increase in the steady-state concentration of radicals in the filled CTA at 320–344 K is associated with the decrease in the efficiency of radical decay and lower values of the parameters $k_{-1} k_3$ and $k_{-1} k'_3$ relative to the parameter $k_1 k_2$ in equations (17) and (18). This is also evidenced by the results of measurement of the temperature dependence of the correlation time of the spin probe rotation.^{99, 100} The effective activation energy of the probe rotary mobility increased from 4.6 kJ mol^{−1} in non-filled CTA to 7.6 kJ mol^{−1} in CTA containing 60 mass % of Aerosil, i.e., filling has a substantial effect on the molecular dynamics and hence on the ratio of rate constants in individual stages of the radical process.

Figure 9 shows that the temperature coefficient of the change in $[\text{R}^{\bullet}]$ variation becomes negative for the highly filled CTA at $T > 340$ K. In CTA containing 30 mass % of Aerosil, an intermediate situation is realised in which only a decrease in the efficiency of radical formation was observed as the temperature was increased. These facts indicate that structural modification upon filling influences most effectively the decay of radicals. It is for this reason that the inversion of the dependence shown in Fig. 9 is observed in the region of transition of the quadratic decay of radicals to the linear one. The mean distance between the filler particles in CTA with 60 mass % of Aerosil is estimated as ~ 10 nm. This distance corresponds to the overlapping of bound-

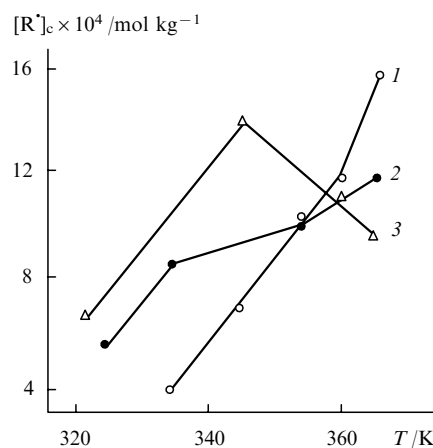


Figure 9. Temperature dependence of the mean radical concentration upon dissociation of DPE in Aerosil-free (1) and Aerosil-filled (2, 3) CTA.¹⁰⁰ Aerosil content (mass %): 30 (2), 60 (3).

dary layers and transition of the entire polymer to a new structural state. Thus, the exit of stable radicals from the cage in the process of thermal dissociation of DPE is rather sensitive to changes in the molecular organisation upon filling of the polymer and can characterise the degree of its structural-physical modification.

V. Conclusion

The kinetics of radical cage reactions demonstrates their clear-cut dependence on the physical structure of solid polymers and filled compositions. A distinctive feature of the processes considered above is their versatile character as regards their possible implementations in diverse polymers and composites over a wide temperature range (77–350 K), viz., from cryogenic to relatively high temperatures. A strong dependence of kinetic parameters on structural factors makes it possible to use such reactions as a sensitive tool for estimating the structural-physical modification of polymers. The results of kinetic studies of radical reactions in polymers can also be of independent significance in designing kinetic models of chemical processes characterised by their spatial-temporal disorder.^{101–103}

Based on the results obtained up to now, it may be concluded that the kinetic regularities of the processes considered reflect physical structures of polymers both on local levels as well as on the scale which is much larger than the sizes of reaction cages. This is evidenced primarily by the results obtained in the studies of the reactions of triplet carbenes. For example, the effect of magnetic field on the kinetics of their low-temperature decay is determined by the distribution of intermediate RP with respect to geometric configurations defined by the nearest cage surrounding. It should be noted that the kinetics of this cage process is rather sensitive to relatively large-scale structural changes which involve the 15–20 nm thick interface layers in filled polymers.

The use of the above 'kinetic' approach in studies of the physical structures of polymers is undoubtedly limited. Today, based on the results obtained, one can speak solely about the possibility of comparative estimation of the extent of structural-physical modification reached in a definite way in a given polymeric material. Thus the dependences of kinetic parameters on the content of a filler may be instrumental in the establishment of polymer transition to a qualitatively different structural state (highly filled polymer) in which the boundary layers begin to overlap. Analogous conclusions about changes in the physical structure may be drawn by measuring yields of definite radicals in the reactions under study. In some cases, kinetic parameters can characterise indirectly the frequencies and energetics of the small-scale molecular mobility.

The difficulties encountered in the attempts to elucidate structural peculiarities based on kinetic data are often due to the fact that the mechanisms underlying the effect of molecular organisation of polymers on the reactivities of the reactants are obscure. Further search for processes which mimic the relationship between the kinetics and the physical structure seems to be in order. The search for the correlation between kinetic parameters and morphological forms of polymers determined by modern physical methods is of great significance for the advance in this direction.

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^c — *Kinet. Catal. (Engl. Transl.)*

^d — *Russ. J. Phys. Chem. (Engl. Transl.)*

^e — *Russ. Chem. Bull. (Engl. Transl.)*

^f — *High Energy Chem. (Engl. Transl.)*

^g — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*

ⁱ — *Russ. J. Struct. Chem. (Engl. Transl.)*

The use of objects and methods of colloid chemistry in nanochemistry

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Abstract. Experimental methods and theoretical concepts of colloid chemistry regarding their possible use in nanochemistry and nanotechnology are considered. The main types of disperse systems which can be regarded as nanosystems are distinguished. Some methods for the preparation of colloidal nanosystems are described. Conditions for extrapolation of phenomenological laws of colloid chemistry to nanosize objects are considered. Examples of self-organised colloidal structures are given. The bibliography includes 205 references.

I. Introduction

According to the classification accepted in colloid chemistry, nanosystems are referred to as ultradisperse colloidal systems with the particle sizes ranging from 1 to 100 nm.^{1–3} This range of particle sizes corresponds to the maximum degree of dispersion at which a colloidal system still preserves one of its basic properties, *viz.*, heterogeneity. According to Reh binder,⁴ the minimum size of the disperse phase particles is about 1 nm (3–5 molecular diameters).

In order to establish the relationship between colloid chemistry and nanochemistry, it seems reasonable to recall the main stages in the development of colloid chemistry. After the pioneering studies by M Faraday (1857), who was the first to obtain stable colloidal solutions (sols) of highly dispersed red gold, it was these systems with the particle sizes of 5–100 nm that were the focus of attention of numerous physicists and chemists during the second half of the 19th century and the beginning of the 20th century. Experimental and theoretical studies of different properties of colloidal solutions led to the establishment of the main laws of colloid chemistry, *viz.*, the law of Brownian motion and diffusion of colloidal particles (A Einstein), the heterogeneous nature of colloidal solutions (R Zsigmondy), sedimentation–diffusion equilibria of dispersions in the gravitation field (J Perrin) and in

a centrifuge (T Svedberg), light scattering (J Rayleigh), coagulation of sols with electrolytes (G Schulze and W Hardy). Studies of properties of colloidal solutions of various substances have led to the establishment of the fundamental principle of the universality of the colloidal state (P Weimarn).⁵

During this period, the leading scientists in the field of colloid chemistry understood well the crucial importance of systematic studies of highly dispersed systems; however, experimental methods of that time did not possess sufficiently high resolution, in particular for the establishment of the structures of ultradisperse particles. Probably it was this circumstance that determined a shift of the peak of studies towards disperse systems with larger particles (foams, emulsions, suspensions, aerosols) and structured systems (gels, coagulation and crystallisation structures).

The appearance of high-resolution methods for the structural studies of substances (NMR, electron and atom-force microscopy, special equipment for measurements of very low surface tensions down to 10^{-3} mJ m⁻², computer simulation, photon-correlation spectroscopy and a number of others) in the second half of the 20th century allowed the initiation of systematic studies of the structures and properties of ultradisperse colloidal systems. Over the last 30–35 years, considerable progress has been achieved in this field; in particular, radically novel classes of ultradisperse systems[†] were obtained and studied. A tremendous experience gained in colloid chemistry in the investigations of ultradisperse systems can effectively be used for the solution of a number of basic and applied research problems of nanochemistry, since these systems are nanosystems[‡] in their essence. However, it should be emphasised that one should be very careful in the extrapolation of laws of colloid chemistry and concepts of the structures of disperse particles and thin layers to the nanosize range. The closer the size of a disperse particle (*d*) to the minimum possible one (*i.e.*, to the nanosize), the stronger become the scale effects, *viz.*, the dependence of various properties on the particle size.^{7,8} Nonetheless, the methods and concepts of colloid chemistry can also be successfully used in nanochemistry with due respect for appropriate restrictions. This problem is rather com-

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[†] A spectacular example of ultradisperse systems may be microemulsions, which are thermodynamically stable systems with the disperse phase composed of droplets several nanometers in diameter.⁶

[‡] To a certain extent, the problem of what to call the particles with the sizes from 1 to 100 nm is terminological rather than that of meaning: the terms ‘nanoparticles’ and ‘nanosystems’ appeared only after the introduction of the SI system of units, *i.e.*, much later than the term ‘ultradispersity’.

prehensive and includes a large set of theoretical and methodological aspects.

The present review pays major attention to the classification of ultradisperse systems, the methods of their preparation, as well as to the theoretical description of processes occurring in these systems.

II. Ultradisperse systems

In the first place, it is useful to discuss what classes (types) of colloidal systems may be regarded as nanosystems. Let us use the classification which is currently accepted in colloid chemistry and relies on certain important characteristics of disperse systems, such as the sizes of the disperse particles d , their dimensionalities (one-, two-, three-dimensional), concentration of particles ν (m^{-3}), the character of interaction between the dispersed phase and the dispersion medium, aggregate states of the dispersed phase and the dispersion medium.^{1–3}

As regards their geometrical parameters, nanosystems and ultradisperse systems are virtually equivalent since in the latter the particle size is in the range 1–100 nm.

Based on their geometrical characteristics (dimensionalities of disperse particles), colloidal nanosystems may be divided into three groups.

1. Three-dimensional (bulk) nanoparticles in which all the three sizes (d_1, d_2, d_3) are in the nanorange. It should be noted that the bulk particles have rather small radii of curvature. This type includes colloidal solutions (sols), microemulsions, nucleation particles formed upon phase transitions of the first type (crystals, drops, gas vesicles), spherical micelles of surfactants in aqueous and non-aqueous media (direct and reverse micelles).

2. Two-dimensional (thin films and layers) nanoparticles in which only one size (thickness) is in the nanorange, while two others (length and width) may be unlimitedly large. These systems include thin liquid films, adsorption mono- and polylayers at the interface (including the Langmuir–Blodgett films),⁹ two-dimensional lamellar micelles of surfactants.¹⁰ Thin liquid films are subdivided into foamy films (between two foam cells), emulsion films (between droplets of direct and reverse emulsions) and wetting films (separating a solid surface and a gas or a liquid). The foamy and emulsion films are referred to as symmetrical films, whereas the wetting films are regarded as non-symmetrical ones. The thickness of symmetrical foamy films stabilised by appropriate surfactants can range from several nanometers (the so-called Newtonian black films)^{11–16} to several tens of nanometers.

3. One-dimensional nanoparticles in which the thickness and width are in the nanorange, while the length may be unlimitedly large. The one-dimensional ultradisperse particles include thin fibres, very thin capillaries and pores, cylindrical micelles of surfactants and nanotubes which much resemble them.^{17,18} This group also includes the wetting line (or the line of three-phase contact), which separates three phases, *viz.*, a solid, a liquid and a gas.^{19,20}

The classification of disperse particles based on their dimensionalities is important not only from the formal viewpoint. In conformity with the Ehrenfest principle, the geometry of particles (the dimensionality of space) has a substantial effect on the character of dependences relating physical parameters.^{21,22} Thus the power index for the distance in the Newtonian gravitation laws and for the electrostatic Coulomb interaction is -2 for three-dimensional space and -1 for two-dimensional space.²²

Yet another remarkable parameter confirming the Ehrenfest principle is the different dependence of the heat capacity of solids at constant volume C_V on temperature T in the range of sufficiently low temperatures. Thus Tarasov^{23–25} showed experimentally that the law of squares ($C_V \sim T^2$) is fulfilled for the lamellar structures (*e.g.*, for graphite and gallium) instead of the Debye law of cubes for isotropic materials whereas the linear dependence ($C_V \sim T$) is observed for the chain structures (of crystals selenium,

HF, BiO_3 and MgSiO_3). The theory of heat capacity of thin films and thin rods (needles) developed by Lifshitz^{26,27} states that at low temperatures the $C_V(T)$ dependences for two- and one-dimensional objects differ substantially from those for three-dimensional crystals.

Yet another example concerns the theory of capillarity. Clerot who put forward in 1743 the hypothesis of the existence of molecular forces suggested that they depend on the distance r in the same way as the gravitation forces ($\sim r^{-2}$). However, this hypothesis contradicted the empirical Juren law (1718) describing the upward movement of wetting liquids in capillary tubes. On the contrary, the Laplace hypothesis (1804)²⁸ of the short-range action of molecular forces ($\sim r^{-1}$) described correctly this phenomenon. It should be noted that the Ehrenfest principle provides the physical substantiation of the Laplace hypothesis. Indeed, the change in the power index from $n = -2$ in the Coulomb law to $n = -1$ in the Laplace hypothesis corresponds, according to Ehrenfest, to the transition from a three-dimensional to a two-dimensional object.

The above-cited regularities reflect changes in a number of physicochemical properties of nanoparticles compared to the corresponding properties of the macrophase. For example, a strong decrease in the melting temperature is observed for nanoparticles of many metals and semiconductors (Ag, Au, Pb, Sn, In, Bi, Ga, CdS).^{29,30} It is also known that the strength of filamentous crystals and fibres can be several times higher than that of macroscopic bodies. Nanosize particles possess an enhanced chemical reactivity manifested in the increase in the rates of chemical reactions involving their particles. This property of nanoparticles is used in the preparation of catalysts. It should also be noted that some phases can appear in nanoparticles which are not revealed in macrosystems. A sufficiently detailed description of special properties of nanoparticles can be found in relevant reviews.^{31–34}

Thus, the Ehrenfest principle has a fundamental significance. However, it has not yet found uses in colloid chemistry, including the theory of surface phenomena, although its potentialities seem to be very large here, especially for the description of nanosystems.

As has been noted, colloidal systems comprise several phases, at least two, therefore, properties of a system depend on the interaction between these phases. Based on the energy of interaction of the disperse phase and the dispersion medium, dispersion systems are divided into two large classes, *viz.*, lyophilic and lyophobic. According to Reh binder,⁴ the formation of stable lyophilic systems results from spontaneous dispersion of a macrophase into particles of colloidal size d . The thermodynamic condition of spontaneous dispersion is described by the expression

$$\sigma d^2 \leq \beta k T, \quad (1)$$

where σ is the surface tension at the disperse phase–dispersion medium interface, β is the coefficient taking into account the particle shape and changes in the entropy of a system due to the involvement of particles in the thermal motion ($\beta = 15–30$), k is the Boltzmann constant and T is temperature. It follows from the condition (1) that the formation of colloidal systems with the particle size of 1–100 nm requires a strong decrease in the surface tension, approximately down to $10^{-2}–10^{-3} \text{ mJ m}^{-2}$. This type of nanocolloids includes microemulsion systems, critical emulsions and micellar systems.^{4,6}

Thus, the range of ultradisperse systems (nanosystems) is very broad and they are very interesting from the scientific viewpoint for reviews, (see, *e.g.*, Refs 35, 36).

III. The formation of ultradisperse systems

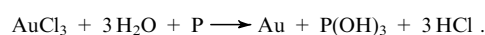
Numerous methods have been developed in colloid chemistry for the preparation of ultradisperse systems allowing a rather fine control over the sizes of particles, their shapes and structures. The Nobel Prize winner Th Svedberg³⁷ proposed to divide methods for the preparation of ultradisperse particles into two groups:

dispersion methods (mechanical, thermal, electrical grinding or spraying of a macroscopic phase) and condensation methods (chemical or physical condensation).

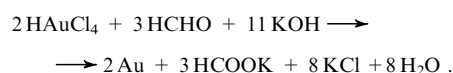
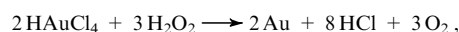
It is impossible to consider all these methods in sufficient detail within the frame of this review; therefore, we will discuss only some examples of chemical methods for the preparation of ultradisperse systems. Historically, it was by these methods that the first highly dispersed colloidal solutions were obtained.

1. Preparation of sols

Systematic development of methods for the synthesis and purification of highly dispersed colloidal systems began in the middle of the 19th century when Faraday prepared stable sols of gold (with the particles 2–50 nm in size) by reduction of a dilute solution of a gold salt with yellow phosphorus.³⁸



Later, Zsigmondy³⁹ developed methods (which became classical) for the synthesis of monodisperse gold sols with a predetermined degree of dispersion by the reduction of gold(III) compounds with hydrogen peroxide and formaldehyde.



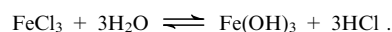
This process proceeds in two steps. In the first step, nuclei of a new phase are formed and then a slight oversaturation occurs in the sol where no new nuclei are formed and only growth of the existing nuclei takes place. Yellow ($d \sim 20$ nm), red ($d \sim 40$ nm) and blue ($d \sim 100$ nm) sols of gold can be prepared in this way.

The invention of an ultramicroscope (1903) which allowed measurement of ultradisperse particles (down to 3 nm in size) gave a strong impetus to the search for new methods for the preparation of sols and studies of their properties. It is worthwhile to note several basic achievements. Svedberg⁴⁰ synthesised highly dispersed sols of alkali metals in organic solvents on strong cooling. Weimarn⁴¹ was the first to establish the conditions under which any substance can be present in the colloidal state: 'Any substance may be obtained in the form of colloidal solution if one succeeds in bringing about the reaction of its formation in a dispersion medium, which dissolves this substance negligibly, at a sufficiently low concentration of reactants.' He prepared sols of several hundred different substances under laboratory conditions.

In the early 1980s, it was found that the solid-phase nanosize particles have special mechanical, optical, electrical and magnetic properties different from the corresponding properties of macro-systems.^{34, 42, 43} This fact determined the wide uses of nanoparticles in different fields of science and technologies.

Numerous methods of synthesis of nanoparticles have been developed to date. Analysis of methods for the preparation of nanoparticles of different nature is reviewed in Refs 31, 34–46. The present review considers only briefly recent methods for the preparation of sols based on condensation reactions.

Hydrolysis of inorganic salts of metals or metal alkoxides resulting in the formation of sols of oxides and hydroxides of the corresponding metals can serve as an example.^{47–51} Thus iron hydroxide sol can be prepared by the reaction



In this approach to sol preparation, it is important to observe thoroughly the reaction conditions; in particular, it is necessary to control strictly pH and the presence of certain organic compounds in the system. Thus Kandori *et al.*⁵² showed that the size of Fe_2O_3 particles resulting from hydrolysis of FeCl_3 depends on the concentration of triethanolamine, isopropylamine and piperazine.

The presence of a large excess energy in disperse systems related to the highly developed interface favours the processes of aggregation of colloidal particles (see Section V). To prepare sols of required dispersity, it is necessary to arrest growth of particles

in due time. To this end, the surface of particles in the disperse phase is deactivated by formation of a protective layer of surfactants^{53–55} or by complex formation.^{56, 57}

As regards control of the shape and size of nanoparticles, highly promising proved to be the synthesis of nanoparticles in microemulsion systems which will be considered in more detail in Section III.3.

2. The formation of micellar systems

Surfactants, organic substances (synthetic or natural) with limited solubility in water, which can adsorb on the interface thereby reducing the interfacial tension, represent unique aspect of colloid chemistry. These compounds have diphilic structures: a surfactant molecule or ion contains a hydrophobic part and a polar group of some kind. The hydrophobic part is a hydrocarbon radical ($\text{C}_n\text{H}_{2n+1}$, $\text{C}_n\text{H}_{2n-1}$, $\text{C}_n\text{H}_{2n+1}\text{C}_6\text{H}_4$, *etc.*) containing from 8 to 18 carbon atoms. Depending on the nature of the hydrophilic group, the surfactants are divided into cationic (these include primary, secondary and tertiary amines and quaternary ammonium bases), anionic (molecules of these compounds contain carboxy and sulfonic groups and others) and non-ionogenic (these surfactants exist in solution in the form of molecules).⁵⁸

The specificity of the behaviour of surfactants in aqueous solutions is related to peculiarities of the interaction between the water molecules and surfactants. According to numerous studies, at room temperature water is a structured liquid and its structure is similar to that of ice but in contrast to ice, water has only near ordering ($r < 0.8$ nm).^{59, 60} Solubilisation of surfactants induces further structuring of water molecules around non-polar hydrocarbon radicals of surfactants, which leads to a decrease in the entropy of the system. As the system tends to the maximum entropy, at a certain concentration called the critical micelle concentration (CMC), the surfactant molecules or ions begin to form spontaneously associates which are called micelles (as proposed by Mac-Ban who discovered them in 1913). The formation of micelles is accompanied by the release of a portion of structured water which is a thermodynamically advantageous process since it leads to an increase in the entropy of the system.

The formation of micelles is usually revealed from changes in some physical property of the surfactant solution (*e.g.*, surface tension, electric conductivity, density, viscosity, light scattering, *etc.*) depending on the surfactant concentration. The magnitude of CMC depends on a number of factors: the surfactant nature, the length and degree of branching of a hydrocarbon radical, the presence of an electrolyte or other organic compounds and pH of the solution. However, the basic factor is the ratio between hydrophilic and hydrophobic properties of the surfactant. The longer the hydrocarbon radical and the weaker the polar group the smaller the CMC.⁸

At concentrations close to CMC, micelles represent nearly spherical formations in which polar groups contact with water, while hydrophobic radicals are directed inwards to form a non-polar nucleus.^{4, 61} Molecules or ions constituting micelles are in dynamic equilibrium with the bulk of the solution. This is one of the reasons for the 'roughness' of the outer surface of micelles.^{61, 62} The degree of hydration of polar groups, the structure of the hydrate layer, and the structure of the internal nucleus depend on the nature of the surfactant.^{63–66}

At concentrations higher than CMC, the formation of several types of differently shaped micelles is possible (Fig. 1): spherical, cylindrical, hexagonal packed and lamellar ones. Thus, micelles may be regarded as one-, two- and three-dimensional nanoobjects. Depending on the surfactant nature, the aggregation number (n) can change from tens to several hundreds, the sizes of micelles will be changing accordingly.⁶⁷

§ Modern concepts of the thermodynamics of surfactant solutions and micellisation processes are considered in sufficient detail in Rusanov's monograph.⁶¹

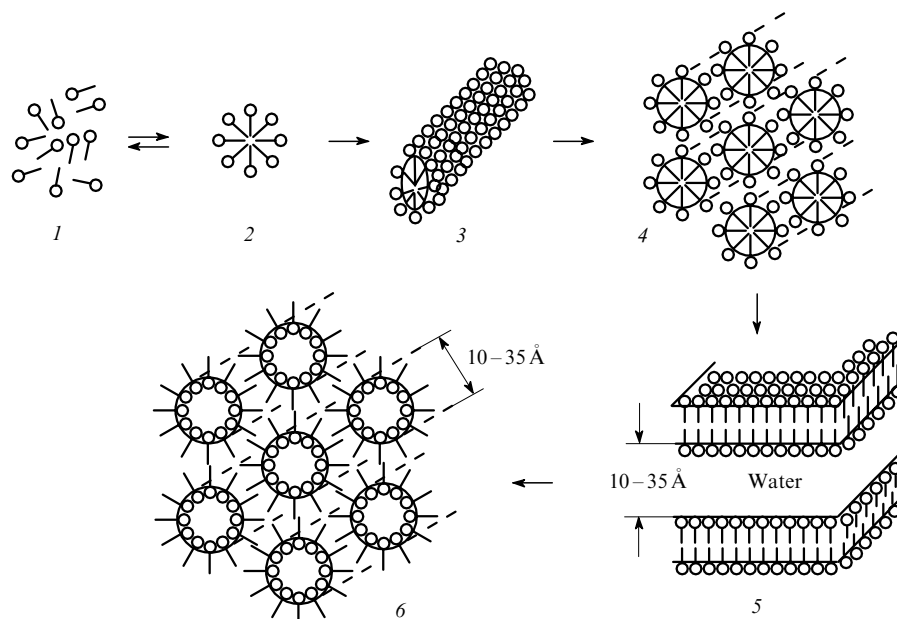


Figure 1. Structures arising in solutions of surfactants: (1) monomers; (2) micelle; (3) cylindrical micelle; (4) cylindrical micelles as packed hexagons; (5) lamellar micelle; (6) water droplets packed as hexagons in the reverse micellar system.

Water-insoluble surfactant molecules with a long hydrocarbon radical and a weakly polar group can be dissolved in non-polar liquid phases. In this case, at a definite surfactant concentration the formation of micelles is also observed and is determined by specific interactions between the polar groups of the surfactant.^{68–71} These are called reverse micelles. The shapes of the reverse micelles are not necessarily the same, this depends on the surfactant concentration.

There are two approaches to the description of micelle formation. According to the first approach (the quasi-chemical model), the micellate formation is considered from the standpoint of the mass action law. The second approach interprets the appearance of micelles as the formation of a new phase.

One of the most important properties of the micellar systems is their ability to solubilise, *viz.*, to increase considerably the solubilities of hydrocarbons in aqueous micellar solutions, or, respectively, of polar liquids in the reverse micellar systems.^{72–74} Solubilisation results in the appearance of thermodynamically stable equilibrium isotropic systems, which are called microemulsions (these systems will be considered in more detail in the next section). Due to numerous factors which influence solubilisation (the nature of contacting phases and surfactants, the presence of electrolytes, temperature), the maximum solubilities of substances in surfactant micelles can vary within very broad limits. It should be noted that upon solubilisation the properties of compounds change largely and can also result in changes in the rates of chemical reactions occurring in these systems. This phenomenon known as the micellar catalysis finds wide uses in chemistry, biology, medicine and various technological processes. For example, the increase in the reactivities of compounds is widely used in the processes of emulsional polymerisation^{75–77} and enzymatic catalysis.^{78–80}

3. Formation of microemulsions

Microemulsions are thermodynamically stable isotropic dispersions of two non-miscible liquids. Upon mixing these liquids, the droplets of one of them stabilised by the interfacial film of a surfactant and a co-surfactant (a low-molecular-mass alcohol) are distributed in the other liquid. The term ‘microemulsion’ was proposed by Schulman⁸¹ who was the first to obtain such systems upon addition of surfactants to a macroemulsion. Microemulsions are regarded as lyophilic disperse systems and may be obtained either by spontaneous dispersion of two non-miscible

liquids as a result of a strong decrease in the interface tension or in the process of solubilisation, as noted above. The thermodynamic stabilities of microemulsion systems are determined by low interface tension which, according to the literature data, may be 10^{-5} mJ m⁻² for ionic surfactants and 10^{-4} mJ m⁻² for non-ionogenic surfactants.⁸² Depending on which phase is dispersed and which is continuous, the microemulsions can be direct [oil in water (o/w)] or reverse [water in oil (w/o)].[¶] In both cases the dispersed phase consists of droplets whose size does not exceed 100 nm.

Microemulsions are, as a rule, multicomponent systems comprising different structures (bilayer, cylindrical or spherical micelles).^{83–85} In the process of micelle formation, optically anisotropic micellar phases, for example, lamellar smectic and hexagonal phases consisting of rod-shaped aggregates of infinite lengths, are formed in addition to the liquid isotropic micellar phases, *i.e.*, microemulsions possess internal microstructures which are currently studied by different methods.^{86–88} In the case where the contents of water and oil in the system are comparable, bicontinuous systems can be formed.^{89, 90}

The properties of microemulsions are largely determined by the sizes and shapes of the dispersed phase particles as well as by rheological properties of interface adsorption layers formed by surfactants. Since the microemulsions are highly mobile and possess large interfaces, they can serve as versatile media for numerous chemical syntheses, including the preparation of solid nanoparticles.

4. The formation of solid particles in microemulsions

In a microemulsion system, the dispersed phase particles continuously collide, coalesce and degrade again, which leads to a continuous exchange of their contents. Collision of droplets depends on their diffusion in the oil phase (for the reverse microemulsion system), whereas the process of exchange is determined by the interaction of adsorption layers of surfactants and the flexibility of the interface (the latter circumstance is crucial for carrying out chemical reactions in such systems).^{91, 92}

Reverse microemulsion systems are often used for the preparation of solid nanoparticles. To this end, two identical microemulsion systems (w/o) containing in their aqueous phases

¶ The term ‘oil’ means a non-polar organic liquid.

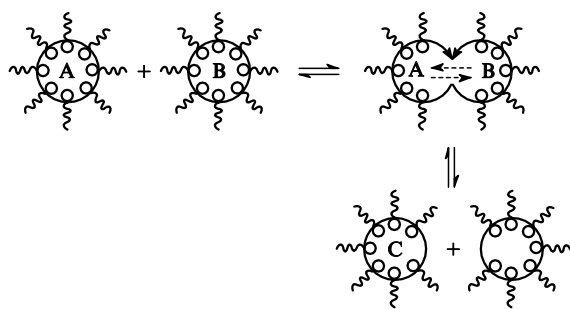


Figure 2. Scheme of a reaction occurring in the reverse microemulsion system.

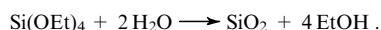
compounds A and B which form a poorly soluble product C in the chemical reaction are mixed. The new compound C is formed in droplets as a result of coalescence (Fig. 2). The sizes of the new phase particles will be restricted by the size of droplets of the polar phase.

Metal nanoparticles can also be obtained by adding a reducing agent (*e.g.*, hydrazine) to a microemulsion containing a metal salt or by bubbling a gas (*e.g.*, H_2 or CO) through this emulsion. It was in this way (reduction of a metal salt by hydrazine) that mono-dispersed metal particles of Pt, Pd, Rh and Ir were obtained with a particle sizes of 3–5 nm.⁹³ An analogous method was applied for the synthesis of bimetallic particles of platinum and palladium.⁹⁴

At present, precipitation reactions in microemulsion systems are widely used for the synthesis of metal nanoparticles,^{95–97} semiconductors,^{98–102} barium, calcium and strontium carbonates and sulfates,^{103–107} monodispersed SiO_2 particles^{108–110} and high-temperature ceramics.^{111–113}

Despite the fact that the mechanism of formation of nanoparticles has not yet been ultimately established, it is possible to identify a number of factors which influence this reaction. These are primarily the ratio of the aqueous phase to the surfactant ($W = [H_2O]/[surfactant]$) in the system, the structure and properties of the solubilised aqueous phase, the dynamic behaviour of microemulsions and the mean concentration of reagents in the aqueous phase. The sizes of droplets in the disperse phase are also influenced by the nature of the surfactants which stabilise the microemulsion system. However, in all cases the sizes of nanoparticles formed in the reaction are governed by the sizes of droplets of the initial microemulsion. For instance, Petit and Pileni⁹⁹ showed that the sizes of CdS nanoparticles increase virtually linearly as the ratio W increases. On the other hand, the sizes of particles obtained in the reverse microemulsion system stabilised by sodium di(ethylhexyl) sulfosuccinate (Aerosol OT) proved to be smaller than those in the system stabilised by the non-ionic surfactant Triton X-100 [polyethylene glycol ($n = 10$) *p*-iso-octylphenyl ether].

Microemulsion systems are also used for conducting hydrolysis. Hydrolysis of tetraethoxysilane in the reverse micellar system stabilised by Aerosol OT can serve as an example.¹¹⁴



It should also be noted that microemulsion systems are used for the preparation of organic compounds, which is important for the creation of new medicinal forms.¹¹⁵

Most of studies in this field relate to the synthesis of spherical nanoparticles. On the other hand, the preparation of asymmetrical particles (filaments, discs, ellipsoids) and a rigorous control of their shapes is also of high scientific and practical interest. Syntheses carried out in the microemulsion systems allowed the preparation of $BaCO_3$ nanofibres¹¹⁶ and asymmetrical nanoparticles of various compounds with unusual magnetic properties.^{117–119}

Highly interesting is the synthesis of nanocomposites consisting of particles of one material (the particle size is 50–100 nm) coated with a thin layer of another material.^{120, 121}

5. Preparation of mono- and polymolecular layers

Surfactants can form monomolecular films on various interfaces: water–air, solid–liquid and liquid–liquid. Such films may be regarded as two-dimensional nanosystems. The surfactant monolayers on the water–air interface were studied by Langmuir who developed an experimental method for the studies of these films (the Langmuir balances).¹²² For this work Langmuir was awarded the Nobel Prize in 1932. Monomolecular films on the surface of liquids may be in the gaseous, liquid and solid states. These states are characterised by different energies of interaction of the surfactant molecules.

Under definite conditions (pH, temperature), the water–air interface is the site of spontaneous formation of highly ordered structures, in which the surfactant molecules (or ions) are arranged in such a way that the polar group is in solution, while the hydrocarbon radical is oriented into the air at a small angle to the interface. The processes of self-organisation in a film are determined by the diphilicity of the surfactant molecules and may be analysed from the viewpoint of interaction of the polar group with the water substrate and interaction of the hydrocarbon radicals with each other.^{122–126}

Chemical reactions occurring in monomolecular films are of considerable interest. By varying the surface pressure it is possible to control the orientation of molecules in the surface layer and influence thereby specifically the occurrence of these reactions. Thus the Langmuir–Blodgett films are used for the preparation of solid nanoparticles of different nature directly in the process of chemical reaction or photochemical reduction of metal salts.^{127–130} Similar processes also occur in biological systems.¹³¹

The films deposited onto the solid surface can form both mono- and polylayers. For example, if a glass plate positioned vertically is drawn from water through a monolayer of barium stearate on its surface, this plate becomes coated with a surfactant layer in which the hydrocarbon radicals are oriented outwards. The result is that the surface of this plate becomes hydrophobic. It can then be covered with the next layer. Hydrophilic or hydrophobic surfaces may be obtained by successive deposition of layers.¹³² The films composed of layers of the same orientation are called the X-films, whereas those with the oppositely oriented layers are called the Y-films. In this way, it is possible to obtain polylayer coatings with thicknesses in the range of nanometers.

IV. The structures and forms of ultradisperse particles

The questions concerning the mechanisms of formation and the structures of nanosize particles are regarded as the most important and essential for colloid chemistry. Indeed, ultradisperse particles are some kind of ‘elementary particles’ of colloid chemistry. The transition from a simple qualitative definition of the concept of disperse particles to the determination of their quantitative parameters and relationships requires detailed elucidation of the structures of ultradisperse particles in different colloidal systems, such as sols, micellar solutions, microemulsions, gels, *etc.*

The early concept of the structures of solid ultradisperse particles was based on the suggestion that their structures are analogous to that of the macrophase of the same substance. However, further studies of the process of nucleation and growth of a new phase showed that depending on crystallisation conditions (the degree of oversaturation or overcooling, the presence of admixtures and a number of other factors), both amorphous and crystalline ultradisperse particles can be formed from solutions.^{133, 134} Back in 1910, Weimarn⁵ found that the shapes of $BaSO_4$ particles formed by crystallisation from solution depended on the degree of its oversaturation. Thus he obtained highly dispersed sols, flocculent structures, well faceted microcrystals

and needle-shaped crystals. The temperature of the synthesis of nanoparticles also plays an important role. For example, nanoparticles of titanium dioxide obtained by the sol–gel method are rod-shaped at low temperature and have the form of bipyramidal crystals at high temperature.¹³⁵ Yet another confirmation of the diversity of forms of nanoparticles is the formation of dendrites upon crystallisation from solutions and melts.¹³⁶

The diversity of forms is due to the fact that the processes of new phase formation (the self-organisation processes) occur under essentially non-equilibrium conditions, and the extent of structural perfection depends on how far the crystallisation conditions deviate from the equilibrium conditions. For example, in the synthesis of diamond from a dense gas phase and plasma, a more perfect structure is formed under more non-equilibrium conditions.¹³⁷

Surfactants present in solution can strongly influence the crystallisation process. Depending on the nature and concentration of the surfactants, they can change the rate of nucleation and growth of nuclei of the new phase, the shape of crystals and distribution of nanoparticles with respect to the size.^{138–141} All these effects are related to the selective adsorption of surfactant molecules or ions on different facets of the crystals formed and consequently to the retardation of growth of some facets compared to others.¹⁴² In addition, the nature of the surfactant also influences the polymorphism of the compounds formed. For example, Füredi-Milhofer *et al.*¹⁴³ showed that crystallisation of calcium oxalate in solutions of octaethylene glycol monohexadecyl ether results in the formation of calcium oxalate monohydrate, whereas in solutions of sodium dodecyl sulfate, dihydrate is formed.

An important feature of the crystallisation processes leading to the formation of nanoparticles is that their shapes cannot be described by the methods of usual geometry. These systems are described using the fractal geometry, since in the case of strong deviations from equilibrium and consequently high values of the driving force of the crystallisation process the instability of the interface leads, as a rule, to the formation of fractal structures.¹⁴⁴

Of interest are the studies reported by Melikhov *et al.*^{145, 146} who showed that highly dispersed primary single crystals are formed first in the mutual crystallisation of ammonium halides and cesium iodide from highly oversaturated vapour. Owing to highly developed interface, the disperse system formed possesses a large energy excess and for this reason it is the site of the occurrence of aggregation processes, which are accompanied by the concrescence of the initial single crystalline particles of approximately the same size. This aggregation results in the formation of pseudo-single crystals.

The processes of formation of ultradisperse systems in the case of metal crystallisation are much more complex and diverse. In the essence, investigation of these processes laid the foundation for a new direction known as the chemistry of clusters.^{147–149} Cluster particles occupy the intermediate position between mononuclear compounds and disperse particles. The metal particles with $d < 30$ nm can be obtained by the methods of gas-phase nucleation, cryogenic synthesis and reactions in polymeric matrices and reverse microemulsion systems.^{150–153}

It should be noted in conclusion that until now there is no sufficiently comprehensive quantitative theory of nucleation and growth of colloidal particles.

V. The application of theoretical concepts of colloid chemistry in nanochemistry

The concepts of colloid chemistry may also be used for the description of nanosystems (ultradisperse colloids). However, this involves rather complex methodological problems. These are due to the intermediate position occupied by the ultradisperse particles between molecules (atoms, ions) and macroscopic bodies (phases).

Both chemical and physical approaches are used for the theoretical description of colloidal systems. This is related to the boundary position of colloid chemistry between chemistry and physics, which exerts a strong effect on its methodology.¹⁵⁴ For example, the chemical approach prevails in studies of the highly dispersed state (including surface layers). Chemical methods are applied for the calculation of the electronic structure of nanoparticles (clusters) and its effect on their catalytic properties,¹⁴⁹ surface forces and Hamaker constants,^{155, 156} as well as for the determination of the constants of adsorption equilibrium using the mass action law.⁶¹ Based on the analogy of a bimolecular reaction and an elementary act of coagulation, the theory of rapid coagulation of sols under the action of electrolytes was developed (M Smolukhovsky, 1916). The theory of electrokinetic phenomena (electrophoresis and electroosmosis) is based on the concepts of electrochemistry on the structure of the double electrical layer and electrocapillary effects.

At the same time, the concepts of molecular physics, chemical thermodynamics and mechanics of continuous media are widely used for the description of relatively large particles and colloidal systems formed by them.

Of particular conceptual interest are the colloidal systems where the progress in the studies has been achieved upon the parallel use of chemical and physical theories, models and methods. A spectacular example of this approach is the investigation of the formation of direct and reverse micelles in solutions of surfactants.

The modern theory of micelle formation has been developed based on two complementary models, *viz.*, the quasi-chemical model (the formation of a micelle resulting from the reversible aggregation reaction) and the model of a phase transition of the second type.⁶¹ Such a conceptual dualism is rather characteristic of the methodology of colloid chemistry. Combination of macroscopic and molecular properties in a single object (colloidal particle, surface layer) was duly appreciated long ago by both chemists and physicists. Thus studies of the capillary and surface phenomena have made it possible to derive first quantitative estimates of the sizes of molecules (B Franklin, T Young) and have led to the discovery of forces of molecular attraction (A Clairaut, P Laplace). Studies of the temperature dependence of the capillary rise of organic liquids made it possible to establish their critical temperatures (D Mendeleev). The Boltzmann constant was calculated from the temperature coefficients of surface tension of pure substances.

Yet another example of the combination of physical and chemical approaches to studies of colloidal systems is the discovery of the effect of adsorption-induced decrease in strength (the Rebinder effect).¹⁵⁷ The modern theory of this effect borrows a number of notions and concepts from the physics of solids and mechanics (dislocation, the concept of tensions in the uppermost part of a fissure, the Griffith theory for the calculation of the critical sizes of nuclei of a crack and others). On the other hand, studies of molecular mechanisms of the Rebinder effect involve inevitably chemical processes and factors, since the decrease in the strength and plasticity of metals, ionic crystals and other solids was caused by the adsorption of the corresponding compounds in the predestruction zone.¹⁵⁷

Phenomenological laws of colloid chemistry established on the basis of molecular physics, thermodynamics and mechanics of continuous media have a fundamental character. However, their direct extrapolation to the ultradisperse field is not, as a rule, sufficiently accurate. This is due to the fact that many properties of substances in the ultradisperse field are substantially dependent on the particle size (d), and changes in properties may be caused by different reasons. For instance, in the range of $d < 1$ μm an increase in the strength of crystals is observed as their diameter d decreases. To an order of magnitude, this ‘threshold’ corresponds to the mean distance between dislocations in non-deformed crystals.¹⁵⁸

Colloidal systems are characterised by a very large specific surface Ω of the dispersed phase

$$\Omega \approx \frac{K}{d\rho},$$

where K is a dimensionless coefficient (for the spherical and cubic particles, $K = 6$), ρ is the disperse phase density. Other most important parameters which characterise colloidal systems are the specific free surface energy σ (surface tension), the surface entropy η and the specific adsorption Γ . For the systems with the moderate degree of dispersion, the surface tension σ is determined only by chemical compositions (the nature) of the dispersed phase and dispersion medium. However, for the nanosystems one has to take into account the dependence of the surface tension on the sizes of dispersed particles.

Because of special importance of the surface tension, let us consider this aspect in more detail. Two approaches are widely used for the analysis of the scale (dimensional) dependence of the surface tension. One of them relates the surface tension to the surface curvature and is used, *e.g.*, for the description of surface properties of droplets, gas bubbles and nuclei of the new phase particles. Tolman¹⁵⁹ proposed the following equation for the description of this relationship:

$$\sigma_r \left(1 + 2 \frac{\delta}{r} \right) = \sigma_0, \quad (2)$$

where σ_r is the surface tension corresponding to the curvature radius r , σ_0 is the surface tension for a flat surface, δ is the thickness of the surface layer of a substance characterised (according to Gibbs) by excess thermodynamic functions. According to a number of estimates, $\delta \approx 1$ nm; therefore, for the nanosize particles and gas bubbles a substantial change (increase) in the surface tension is observed. For this reason, the corresponding corrections considering the dependence $\sigma = f(r)$ should be made in all fundamental laws of colloid chemistry, *viz.*, the Laplace law of capillary pressure, the Young law of contact angles of wetting, the Kelvin law of the saturated vapour pressure over a curved surface and others. The dimensional factor plays a rather substantial role in the formation of nucleation particles during phase transitions. Indeed, the classical thermodynamic relations which determine the critical size of the nucleus of a new phase include the surface tension for the surface of small curvature, though it is in the nucleation particle that the surface curvature is the largest.

Let us clarify this statement with the following example. The critical size of the new phase nucleus r_c in the homogeneous formation resulting from the phase transition of the first type is determined in the Gibbs theory by the equation

$$r_c = \frac{2\sigma T_m}{Q_m \Delta T}, \quad (3)$$

where T_m and Q_m are the temperature and heat of phase transition and ΔT is the deviation of temperature from T_m . Thus, rather considerable overcoolings ΔT are required for the crystallisation of very small droplets of liquid metals, starting approximately from 5 nm. For instance, the values of ΔT for mercury, tin, copper and platinum were found to be 77, 118, 236 and 370 °C, respectively.¹⁶⁰ The simplest rationale is the increase in the surface tension as the curvature radius decreases [Eqn (2)], which leads to the corresponding increase in the overcooling ΔT (at a fixed value of the droplet size r_c).

A different approach to the description of special properties of ultradispersed objects (thin liquid films) is used in the concept of disjoining pressure Π introduced by Deryagin.¹⁹ The disjoining pressure is the difference between the pressure P_H inside the film of thickness H and the pressure in the bulk phase P_0 of the same substance at the same values of temperature and chemical potentials as in the thin film.

$$\Pi = P_H - P_0. \quad (4)$$

The most important feature of thin films is that their thickness H is commensurable with the surface layer thickness δ . The overlapping of the surface layers of two contacting phases (for $H < \delta$) makes an additional contribution to the free energy of the film.

The concept of disjoining pressure has been developed in sufficient detail and is widely used nowadays for the description of many phenomena. Thus the concept of disjoining pressure forms the basis of the theory of stability of colloidal solutions [the Deryagin–Landau–Verwey–Overbeek theory (DLVO)].^{161–163}

Certain problems also arise in the description of wetting of solids with nanosize droplets. In these cases, the equilibrium contact angle of wetting Θ_r depends on the linear tension $\varkappa$. The corresponding equation is

$$\cos \Theta_r = \cos \Theta_0 - \frac{\varkappa}{\sigma r}, \quad (5)$$

where Θ_0 is the equilibrium angle of a droplet at a large curvature radius (≥ 0.1 mm) and r is the radius of the droplet base.

This relation, which is analogous to the Laplace law of capillary pressure $P_r = 2\sigma/r$, was obtained for the first time and confirmed experimentally in measurements of forces on the wetting line in the plane of a bubble base on a solid support.¹⁶⁴ The contact angle Θ_r for a droplet or a bubble with a small radius r is determined from the conditions of mechanical equilibrium on the three-phase contact line (TPL).^{165, 166}

The direct confirmation of the dependence of Θ_r on the linear tension was obtained for microdroplets of organic liquids on asbestos filaments.¹⁶⁷ According to different estimates, the magnitude of linear tension is $\sim 10^{-7}$ mN.¹⁶⁶ Therefore, this can make a noticeable contribution to the magnitude of contact angles (for liquids with the surface tension $\sigma \approx 50$ – 100 mN m⁻¹) only in the case of nanosize droplets ($r \sim 10^{-9}$ m).

The influence of linear tension becomes rather substantial in the heterogeneous formation of the new phase nuclei, *e.g.*, upon vapour condensation on wetted solid substrates. Thermodynamic analysis¹⁶⁶ provides the following equation for the work of a nucleus (droplet) formation as a spherical segment

$$A = \frac{PV}{2} + \frac{\varkappa l}{2}, \quad (6)$$

where P is the capillary pressure, V is the droplet volume, l is the length of the TPL. Relation (6) may be regarded as a generalised equation with the aid of which one can calculate the work of formation of the new phase nucleus in the nanosize range (it is for this purpose that the linear tension $\varkappa$ is introduced). In the case of a spherical droplet $\varkappa = 0$, and relation (6) is transformed into the equation which describes the work of homogeneous formation of the new phase nuclei (A_0).

In order to calculate the work of heterogeneous formation of the new phase nucleus A_h , use is made of the well known Volmer equation¹⁶⁸

$$A_h = A_0(2 - 3 \cos \Theta_0 + \cos^3 \Theta_0). \quad (7)$$

Finally, for $V = 0$ equation (6) describes the work of formation of a two-dimensional nucleus ($A = \varkappa l/2$).

The above-cited examples of extrapolation of some laws of colloid chemistry to nanodispersed objects should be regarded only as a first approximation. The basic reason for the limited action of these laws, even with the consideration of the mentioned corrections, consists in peculiarities of the structure of nanosystems (see Section III). The complexity and non-triviality of the problems arising in this extrapolation will be explained by the example of two nanoobjects which are widely distributed in technological and natural processes: the surface layer of a liquid and LTC.

At the interface of a pure liquid and a gas phase the surface layer (SL) has a very small thickness (δ) which is of the order of several molecular layers (far from the critical temperature), *i.e.*, it represents formally a two-dimensional nanoparticle with two

macroscopic sizes (length and width) and one nanosize (thickness). Such a definition follows from the classical Young–Laplace theory; it is also confirmed by calculations based on macroscopic theories. The Gibbs theory considers the SL of a substance as an independent phase, the thermodynamic parameters of which differ from analogous parameters of the bulk phase of the same substance. Evidently, it is for this reason that the structure of SL of a liquid will differ from the structure in the bulk.

Until recently, the SL structure could not be studied in detail because of the absence of adequate experimental methods. Only in the last 5–7 years has the improved method of small-angle scattering made it possible to obtain reliable information about the SL structure of different liquids (mercury, gallium, alkanes starting from $C_{16}H_{34}$ and some others). It was found for all the compounds studied that their SL represents a two-dimensional quasi-crystalline structure at temperatures several degrees higher than the melting temperature T_m . The thickness of SL is estimated to be 1–2 molecular (atomic) diameters. It was established that the parameters of a two-dimensional crystal differ from the parameters of the lattice of a ‘bulk’ crystal of the same substance.^{169, 170}

These experimental data confirm the recent network model of the surface layer of a liquid,^{171–173} according to which it contains nanoparticles of the solid phase. They form a structure (‘network’) which determines the appearance of the surface tension of a liquid. The model predicts rather simple correlations between the surface tension and the heat of melting, which are in good agreement with experimental data for liquid metals and liquefied inert gases.

These results seem to be of principal significance. It follows from them that the surface nanolayer of a pure liquid has in fact an aggregation state different from the state in the bulk. This confirms one of the initial postulates about the thermodynamics of the surface Gibbs phenomena which states that the SL is an independent phase.^{171, 174}

On this basis, the process of SL formation may be regarded as the phase transition liquid–two-dimensional solid.¹⁶² In the framework of this model, the surface tension σ_m is proportional to the heat of melting Q_m near the melting temperature T_m . It thus follows that

$$\sigma_m = Q_m \rho_s \delta = Q_{sf}, \quad (8)$$

where ρ_s is the solid phase density and Q_{sf} is the heat of SL melting per surface unit. In the first approximation, the thickness of the SL (δ) is equal to a (a is a parameter of the crystal lattice of a given compound). Figure 3 shows that the dependence $\sigma_m = f(Q_m)$ is very well respected for many liquid metals and liquefied inert gases. The thickness of the SL for liquid alkali metals, other melts and liquefied gases corresponds to four, two and one monolayers, respectively.

The model of the solid SL makes it also possible to calculate the temperature coefficient of surface tension $-d\sigma/dT$ from the

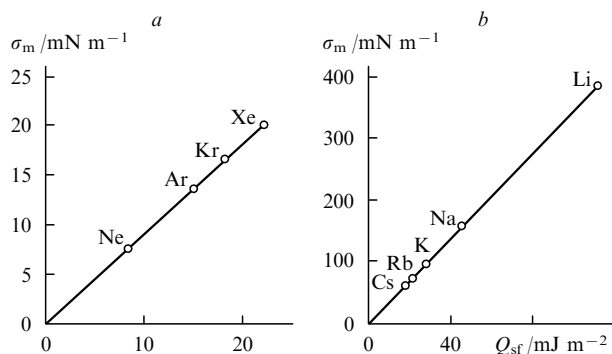


Figure 3. Correlation of the surface tension σ_m near the melting point with heat of melting Q_{sf} : (a) liquefied inert gases, (b) alkali metals.

entropy of melting $\Delta S = Q_m/T_m$. Calculations of the coefficients of surface tension for many liquid metals give a rather close correspondence to experimental data.^{171, 172}

Let us consider yet another example of the insufficiency of introduction of additional thermodynamic parameters (the disjoining pressure Π , the linear tension κ) for the development of a comprehensive theory of colloidal nanosystems. In three-phase systems, the most important nanoobject is the three-phase contact line. This appears upon wetting, capillary flow, adhesion of liquids, spreading of drops over the surface of solids, condensation of vapours on supports and other phenomena. In these processes, the TPL is the front boundary of the liquid meniscus. Besides the term ‘three-phase contact line’ (TPL), the term ‘wetting line’ is used in a number of cases. As noted above, the linear tension describes special properties of TPL. Various theoretical models which consider the influence of the linear tension κ on the contact angles Θ [see Eqn (5)] include in the implicit form the suggestion that the wetting line is a regular circumference, *i.e.*, it has the same curvature $1/r$ along the entire length. An analogous assumption is also used, *e.g.*, in the theoretical description of spontaneous spreading of a drop of wetting liquid over a solid or liquid surface,^{7, 175, 176} flows in capillaries and porous media,^{177, 178} *etc.*

However, precision studies of the contour of drops of various liquids on solid supports (electron microscopy, laser interferometry) led to the conclusion about a totally different form of the wetting line. In the nanoscale, it represents an irregular alternation of protrusions and depressions, which are respectively ahead of or behind the mean position of the ‘round’ wetting line, *i.e.*, it is composed of small sites of positive and negative curvature.

This result is rather important for the development of a microscopic theory of wetting. In the first place, it shows that the movement of the wetting line upon the drop spreading should not be regarded as a smooth expansion of the wetted area within the limits of the entire contour (this assumption is used in the hydrodynamic theory of spreading).^{15, 176} A different mechanism of motion appears to be more probable, *viz.*, the fluctuational formation of leading menisci in the radial direction and subsequent tangential flow of a liquid under the action of the capillary pressure created. This mechanism of the wetting line dislocation requires a much lower activation energy than that based on the simultaneous spreading of a drop over the entire perimeter. Such a movement of TPL has much in common with the sliding of edge dislocations in crystals;¹³⁷ therefore, one can effectively use the corresponding models (formation of kinks, their expansion, *etc.*) for its description. At the same time, good prospects are open for the use of methods of fractal geometry for the description of these objects.

VI. Self-organised colloidal structures

A fundamental property of dispersed systems is their capacity for a gradual evolution. This evolution is associated with the nature of the colloidal (dispersed) state and primarily with the thermodynamic non-equilibrium of most colloidal systems. The excess of free energy, which is determined by the presence of a highly developed interface separating the dispersed phase and dispersion medium, stimulates different processes (physical, physicochemical) leading to a decrease in the Helmholtz free energy F .

Without consideration of the chemical component, the variation of the Helmholtz free energy dF at a constant temperature is

$$dF = -TdS + d(\sigma\Omega), \quad (9)$$

where Ω is the interface magnitude.

The thermodynamic condition of evolution $dF < 0$ may be created in energy- and entropy-based ways. The former is characterised by changes in the second member of Eqn (9). This may be attained by decreasing the interface separating the dispersed phase and dispersion medium ($\sigma d\Omega < 0$) and by decreasing the inter-

facial free surface energy (the surface tension) ($\Omega d\sigma < 0$). Upon the decrease in the interface, an increase in the mean sizes of particles d takes place, *i.e.*, the distribution of particles over their sizes, which is fixed directly at the moment of their formation, is shifted with time towards the larger particles. The mechanisms of this process may be completely different: coalescence of droplets in emulsions and of gas bubbles in foams upon their direct contact, isothermal distillation of the disperse phase particles in conformity with the Kelvin law, the Ostwald ripening of solid particles. As a result of these processes, the solid particles can become so large that they lose their sedimentational stability. Ultimately, these processes can lead to the partition of a dispersed system into two macrophases.¹⁷⁹

The decrease in the specific free surface energy $d\sigma < 0$ also occurs upon the interaction of the dispersed particles through the dispersion medium film, as well as upon the loss of aggregation stability by the system in the process of coalescence. The theory of sol stability (the DLVO theory)¹⁶³ considers in the first approximation the interaction of colloidal particles as the sum of dispersion (attraction) and electrostatic (repulsion) interactions which take place upon overlapping of the ionic atmospheres due to the approach of sol particles to each other. In the case where the radius of the dispersed particles is much larger than the thickness of ionic atmosphere, the energy of interaction of colloidal particles $U(h)$ may be expressed as

$$U(h) = \frac{Bc_0kT\gamma^2}{\kappa} \exp(-\kappa H) - \frac{A^*}{12\pi H^2}, \quad (10)$$

where B is a numerical coefficient, c_0 is the electrolyte concentration in the system, $\gamma = \tanh(ze\phi_0/4kT)$ (z is the valence of the counterion and ϕ_0 is the thermodynamic potential of the solid surface), κ is the magnitude of the reciprocal thickness of ionic atmosphere in the Debye–Hückel theory, $\kappa = (\epsilon\epsilon_0kT/2z^2e^2c_0)^{-1/2}$ (ϵ is the dielectric constant of the medium, ϵ_0 is the dielectric constant equal to 8.85×10^{-12} F m⁻¹), H is the thickness of the dispersion medium film between particles, A^* is the Hamaker complex constant characterising the interaction of contacting phases.

It follows from the DLVO theory that if the energy barrier related to the electrostatic repulsion of particles (E_{el}) is substantially higher than the energy of thermal motion (*i.e.*, $E_{el} \gg kT$), then the system is stable to aggregation, and no enlargement of particles occurs.

If $E_{el} \ll kT$, then each collision will lead to the formation of an aggregate, and the rate of formation of aggregates will be limited by the rate of their diffusion in the dispersion medium. This process is called rapid coagulation (M Smolukhovsky, 1916). The parameter which characterises the process of rapid coagulation is the coagulation period (τ), *viz.*, the time during which the concentration of particles v_0 decreases by a factor of two. According to the Smolukhovsky theory,

$$\tau = \frac{3\eta}{8kTv_0}, \quad (11)$$

where η is the viscosity of the dispersion medium. For the rapid coagulation, the value of τ does not usually exceed a few seconds.

Upon a decrease in the electrolyte concentration, the efficiency of collisions decreases and only a portion of them leads to the formation of aggregates. This is the case of the so-called slow coagulation (N Fuchs, 1934). In conformity with the Fuchs theory, the decrease in the rate of aggregate formation is associated with the presence of a barrier in the dependence of potential energy on the distance between the centres of particles.¹⁸⁰ The theoretically predicted dependences of the coagulation rate on concentration, as well as the ratio of rates as a function of the coagulating ion charge are in a satisfactory correlation with experimental results.

The coagulation of sols yields aggregates, the fractal dimensionality of which depends on the coagulation type. For the aggregates formed under the conditions of slow coagulation, the

fractal dimensionality proves to be higher^{181–183} than for the aggregates formed under the conditions of rapid coagulation, which points to a higher degree of their organisation.

Analysis of Eqn (10) showed that at sufficiently large values of H a minimum can be observed on the curve of the dependence of interaction energy of particles on the distance. The interaction of particles at large distances, the so-called far interaction, leads to the formation of ensembles possessing the phase stability. Such ordered formations are called periodic colloidal structures.¹⁸⁴

A spectacular example of the periodic structures are the Schiller layers, *viz.*, the structures formed in sols of iron hydroxides, vanadium oxides and some others whose particles have the anisometric forms. At low sol concentration, the particles form horizontal layers upon sedimentation separated from each other by several hundred nanometers.¹⁸⁵ The increase in the sol concentration leads to the spindle-like aggregates which are called tactoids. In this case, the dispersed particles are arranged nearly in parallel to the spindle axis, while the distance between them is decreased to tens of nanometers. The dispersed particles can also be oriented near a solid support.^{135, 186}

The periodic colloidal structures include also the Liesegang layers and rings,¹⁸⁷ which were apparently the first examples of the self-organised structures studied. Let us consider these objects in more detail.

The Liesegang rings (1896) can be prepared in the following way. A drop of 15% solution of AgNO₃ is placed on a film of the gelatine gel which has been pre-impregnated with 0.4% potassium dichromate solution. The silver salt diffuses gradually into the gel. This results in the precipitation of silver dichromate. The precipitate does not form a continuous zone around the drop but is in the form of concentric rings separated by transparent clear areas.

Usually, the Liesegang rings appear when a concentrated salt solution diffuses through a gel which contains another electrolyte at a lower concentration. The chemical reaction results in the formation of a salt of a poorly soluble compound which is precipitated in some periodic way.^{187–190} The precipitate can form not only the concentrated rings but also segments and radial formations.^{191, 192} It should be noted that despite the long time which has passed since the discovery of Liesegang rings, a sufficiently complete theory of their formation has not been developed until now. It should be mentioned that this phenomenon is of a considerable interest not only for colloid chemistry but also for other sciences, *e.g.*, biophysics. Indeed, the Liesegang rings are similar to ring structures which result from the autowave processes occurring in unidimensional systems (thin layers).¹⁹³ In such ‘distributed’ systems, the periodic wave structures appear due to diffusion undisturbed by convective fluxes, *i.e.*, owing to the distribution of concentration waves. The same conditions are necessary for the formation of Liesegang rings. In the case of the reaction under discussion, one of the possible reasons for the appearance of Liesegang rings may be formation of colloidal particles of silver dichromate which coagulate because of the excess of one of the reagents.

The processes of self-organisation are observed in the disperse systems under external impacts as well. Thus it was shown in a number of studies^{194–198} that the aggregation of initial particles with the formation of ordered structures is possible in the shear flow of suspensions.

The above-cited examples refer to the ordered colloidal nano-systems with relatively large sizes of particles.

Let us consider now another extreme case, *viz.*, the self-organised nanosystems in which the size of dispersed particles is only slightly larger than the molecular size. These systems include, *e.g.*, aqueous solutions of surfactants. The possible cases of self-organisation of the surfactant molecules are shown in Fig. 4; they include adsorption layers of surfactants at the interface, as well as direct and reverse micelles.

Indeed, the close-to-saturation layers of surfactants at the interfaces water–air, water–oil and polar solid surface–surfactant solution can have a rather high degree of ordering at which all

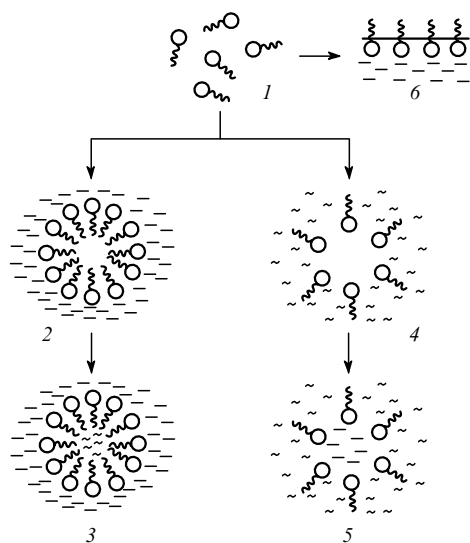


Figure 4. A scheme of the formation of organised structures in solutions of surfactants: (1) surfactant solution; (2) direct micelle in aqueous solution; (3) solubilisation of a non-polar liquid by the direct micelle; (4) reverse micelle in a non-polar liquid; (5) solubilisation of the polar phase by the reverse micelle; (6) adsorption layer of the surfactant at the aqueous solution – air interface.

the surfactant molecules (ions) are oriented perpendicular to the interface in a way ensuring the contact of the polar groups of the surfactant with the polar phase. It should be specially noted that the formation of self-organised biologically active structures on the water surface plays an extremely important role in biological evolution. Numerous data and calculations show that the surfaces of oceans (seas) are the most favourable regions for the appearance of Protozoa.¹⁹³

Another class of self-organised colloidal nanostructures of minimum size includes the direct and reverse spherical micelles of surfactants. The ordering of micelles is characterised by the same orientation of the surfactant molecules (ions) in the radial direction from the centre of the micelle to its outer surface, on which the functional groups similar in their nature to the dispersion medium (water or an organic liquid) are positioned. The self-organised nanostructures of this type also include lamellar and cylindrical micelles, bilayers of surfactants and vesicles.

The factors favouring the formation of self-organised structures of surfactants depend to a considerable extent on the nature of the liquid phase or the nature of the solid substrate (when considering the processes of adsorption of surfactants from solutions on solid surfaces). In aqueous solutions of surfactants, the processes of self-organisation are determined by the general increase in the entropy of the system $dS > 0$ which is the sum of changes in the entropy of the dispersed phase dS_d and in the entropy of the dispersion medium dS_m . In this case, the local decrease in the entropy of the surfactant molecules in the processes of adsorption on the interface aqueous solution – air and micelle formation is compensated by the increase in the entropy of the water molecules so that the total change in the entropy of the system $dS > 0$.^{61, 199–202}

On the contrary, the appearance of micelles in the oil phase, as well as the adsorption of surfactants at the interface water – oil or on a polar solid surface are determined by changes in the enthalpy of the system due to the interaction of the polar groups of surfactants with each other in the nuclei of reverse micelles or because of the interaction of the polar groups of surfactants with a polar solid surface or a polar solvent.^{203, 204}

It should be noted that the processes of self-organisation of surfactant ions can also be observed in gels.²⁰⁵

Thus, the most important feature of the evolutionary processes in colloidal systems consists in that they often lead to the appearance of ordered structures of different scale (nano-, meso-, and micro-macrostructures). These structures may be two-dimensional and three-dimensional, while their size can change from several nanometers to hundreds of nanometers. Such structures are rather widely distributed. They are of a considerable applied and scientific interest, being convenient models of a number of biophysical and biochemical systems.

VII. Conclusion

The nanoparticles considered in colloid chemistry are the ultra-disperse particles. Among the ultradisperse systems a special place is occupied by the systems in which particles have a specific colloidal nature: they include micellar systems, microemulsions, adsorption layers of surfactants at the interface and the Langmuir – Blodgett layers.

The methods for the preparation and studies of ultradispersed systems developed in colloid chemistry may be used rather efficiently in nanochemistry and nanotechnology. In many cases, the methods of colloid chemistry make it possible to regulate rigorously the sizes, shapes, compositions of ultradispersed particles and properties of the structures formed by them. The theoretical concepts of colloid chemistry concerning the surface phenomena, stability and evolution of disperse systems combined with the models used for studies of the thermodynamics of irreversible processes and synergism may also be applied successfully to the nanodisperse systems.

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Dynamic and stimulated nuclear polarisation in photochemical radical reactions

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Abstract. Highly sensitive time-resolved magnetic resonance techniques based on the effect of variable radio-frequency and switched constant magnetic fields on the nuclear polarisation of diamagnetic products of radical reactions are considered. The applications of these methods to the investigation of short-lived radical intermediates (radical pairs, biradicals, free radicals and radical ions) formed in photochemical reactions in homogeneous and molecular-organised media are discussed. The bibliography includes 148 references.

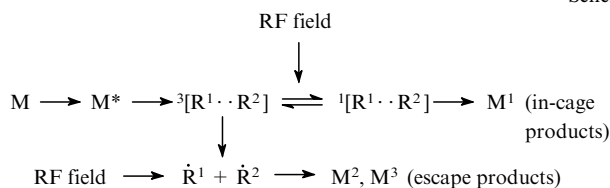
I. Introduction

The review is devoted to the use of new time-resolved magnetic resonance techniques based on the detection of nuclear polarisation of diamagnetic products of radical reactions for the study of spin dynamics and chemical kinetics of short-lived radical species (free radicals, radical pairs and radical ion pairs) in photochemical radical reactions. The demand for investigation of fast photochemical reactions in solutions has stimulated the appearance and extensive development of methods for the detection of short-lived radical species, for example, laser flash photolysis, time-resolved EPR, reaction yield detected magnetic resonance methods (RYDMR), *etc.* The progress in the investigations into the mechanisms of photochemical radical reactions is largely associated with the use of magnetic resonance[†] because these methods provide information on the structure of radicals, the rates of chemical reactions, electron exchange interaction, the parameters determining the mobility of radical species in solutions.

Methods based on the application of variable resonance magnetic fields have been greatly developed during the last two decades.^{1–12} A radio-frequency (RF) resonance field induces nuclear polarisation of in-cage (M^1) and escape (M^2 , M^3) diamagnetic products of a photochemical reaction. Polarisation arises either upon RF-induced changes in the singlet–triplet conversion rate in radical pairs (selectively with respect to the

orientation of nuclear spins) or upon electron or nuclear transitions in the free radicals R^1 , R^2 (Scheme 1). The magnitude and the sign of nuclear polarisation induced by an RF field depend on the field frequency and on the type of resonance transition (nuclear or electronic) to which this frequency corresponds.

Scheme 1



There are several methods for detecting magnetic resonance spectra of short-lived radical species.

(i) Stimulation of nuclear transitions in polarised intermediate short-lived radicals with simultaneous recording of the NMR spectra of diamagnetic products.^{13–18} This method was first proposed and implemented in a study by Sagdeev *et al.*¹³ and was developed further by Trifunac *et al.*^{14–18} An obvious advantage of the method is high sensitivity (below 10^8 spins in the sample) and simplicity of line assignment — the lines of the product detected by NMR correspond to a particular nucleus in the radical precursors. The main shortcoming of the method is that its scope is limited to radicals the lifetimes of which are not shorter than several microseconds.

(ii) The method of dynamic nuclear polarisation (DNP). Pumping of electron transitions in the intermediate short-lived radicals gives rise to nuclear polarisation, which is transferred to diamagnetic products after radical recombination.^{12, 19–22} The dependence of the signal intensity in the NMR spectrum of diamagnetic products on the external magnetic field is an EPR spectrum of the intermediate radicals. This method provides information on the mechanism of electron–nucleus interaction in short-lived radicals (contact or dipole–dipole); it opens the way for determining the relaxation times, the signs and the magnitudes of hyperfine coupling (HFC) constants and for investigation of the kinetics of these radicals in solution.

(iii) The method of stimulated nuclear polarisation (SNP). The effect of an RF field with a specified frequency on an ensemble of

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[†] The sensitivity of EPR (10^9 spins in a sample) does not always suffice for the investigation of fast radical processes.

radical pairs changes nuclear polarisation in the products formed.^{12, 23–25} By investigating the dependence of nuclear polarisation of the diamagnetic products on the frequency of the saturating field, one can gain information on the EPR spectrum of the intermediate radical pair, exchange interaction, pathways to diamagnetic products, *etc.*

II. Experimental implementation of the methods

For recording the spectra of short-lived radicals, it was necessary to devise instruments which either produce a variable resonance magnetic field at radio frequency or ensure the possibility of switching an external magnetic field directly during a radical reaction with simultaneous recording of the NMR spectra of diamagnetic products. Coupling of a resonator or an oscillator circuit with the probe of a standard NMR spectrometer was a complicated engineering problem. This was done by Sagdeev *et al.*¹³ in the first experiment on recording the NMR spectra of short-lived radicals. In scanning the resonance lines, the frequency sweep of the RF field was accomplished manually; due to the restrictions in the frequency range of the resonance circuit of the NMR spectrometer, only one resonance line was detected. The separate pumping of resonance transitions in radical pairs and recording the NMR spectra of the reaction products proved to be an easier procedure (Fig. 1). A fast-flow system is normally used to transfer the sample into the photolysis cell. A liquid is injected into the cell through a thin Teflon capillary either using a pump^{17, 20, 26} or under a gas pressure.¹² The flow rate of the liquid should be such that the time it takes to transfer the sample from the reaction vessel to the probe of the NMR spectrometer be shorter than the nuclear relaxation time of diamagnetic products, *i.e.* this should require fractions of a second. An original setup for detecting SNP in weak magnetic fields of about 10.0 mT has been developed.²⁷ The transfer of a sample from the magnetic field in which the photochemical reaction took place to the probe of the NMR spectrometer was performed using the pneumatic system of the probe. The frequency of pumping of electron transitions (300 MHz) was equal to the resonance frequency of the NMR spectrometer. The limitations of this method include the use of only one resonance frequency of an RF field.

The magnetic flux chosen (B_0) is largely determined by the goals of the experiment. The resonance frequency employed in existing experimental setups ranges from 50 MHz to 10 GHz.

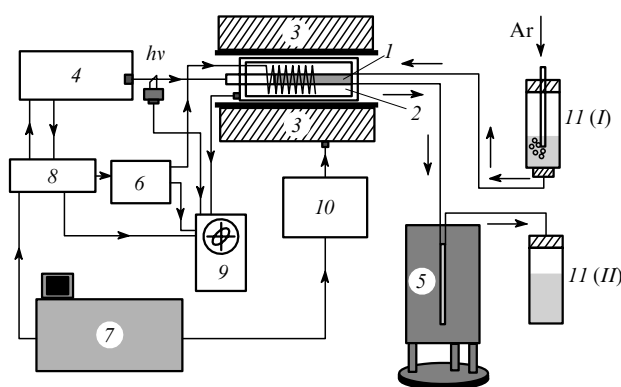


Figure 1. Block diagram of the setup for the study of SNP: (1) photolysis cell with a sample; (2) RF resonator or oscillating circuit; (3) electro-magnet; (4) laser (308 nm); (5) superconductive magnet and the probe of a Bruker MSL-300 NMR spectrometer (300 MHz); (6) RF generator; (7) control computer of the NMR spectrometer; (8) pulse generator; (9) an oscilloscope; (10) power supply of the magnet and B_0 sweep; (11) fast-flow system consisting of a vessel (I) with the initial substances (argon feed under a pressure of ~ 1.5 atm) and a vessel for the collection of the reaction products (II).

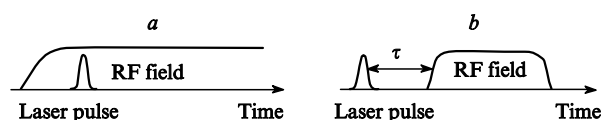


Figure 2. Schematic illustration of the two methods for recording the spectra: continuous (a) and pulse (b).

In pulse methods²⁸ (Fig. 2), the dependence of the intensity of NMR spectra on the time delay (τ) between the laser pulse and the RF pulse is studied. The main difference between the pulse and steady-state methods is as follows. When the continuous variant is used, radical pairs and the intermediate short-lived radicals exist throughout their lifetimes under the influence of an RF field, which induces the singlet – triplet conversion in radical pairs or the DNP. The use of pulse modification provides a new, in principle, opportunity to expose separate sub-ensembles of radical pairs (or radicals) with a particular lifetime to an RF field. The main advantages of the pulse variant over the steady-state method include differentiation of geminate and diffusion pairs by measuring the SNP for different delays τ ; separation of the contributions of SNP and DNP to the RF field-induced nuclear polarisation; the possibility of obtaining information on the pattern of distribution of radical pairs and radicals over lifetimes. In the case of pulse method, time resolution is determined by the rise times of the microwave pulse and the laser pulse and equals 20–30 ns. High time resolution can be achieved by using either cavities with low Q-factors or cavities with high Q-factors but with a higher coupling constant between the resonator and the generator.²⁹ Upon mathematical processing of the data, the time resolution of the method can be improved to 5 ns.²⁷

A substantial drawback of the above methods of recording the spectra is the necessity of using large samples. The use of deuterated solvents markedly increases the cost of the experiment; however, this problem can be solved by taking solvents containing no protons (CCl_4 , C_6F_6 and so on) or by recording the spectra for other nuclei (^{13}C , ^{31}P , ^{19}F and so on.). In the case where the NMR chemical shifts of the solvent and the compound under study differ by several ppm (at least, by 1 ppm), the signal of the solvent should be suppressed.

III. Dynamic nuclear polarisation

The DNP effect means that saturation of the electron levels of free radicals in an external magnetic field gives rise to a non-equilibrium nuclear polarisation.^{30, 31} A radio-frequency resonance magnetic field makes the occupancies of the electron levels equal and thus creates non-equilibrium occupation. Cross-relaxation transitions caused by hyperfine coupling of an electron with the nucleus are directed at restoring the thermal equilibrium between the electron levels. However, since cross-relaxation processes are accompanied by inversion of nuclear spins, polarisation arises on the radical nuclei,

$$p = \xi s f \frac{\gamma_e}{\gamma_n},$$

where, the parameter ξ is determined by the mechanism of the electron – nucleus coupling, $s = (S_0 - \langle S_z \rangle) / S_0$ is the saturation factor of the electron spin system, f is the leakage factor determining the fraction of nuclear relaxation occurring without participation of electron spins, and γ_e and γ_n are gyromagnetic ratios of the electron and nuclear spins. For contact interaction [the change in the total spin of the electron and the nucleus (Δm) is equal to zero], $\xi = 1$, while for dipole interaction ($\Delta m = 2$), $\xi = -1/2$. Figure 3 illustrates qualitatively the mechanism of formation of the DNP upon non-equilibrium electron polarisation of a radical with two equivalent magnetic nuclei ($I_1 = I_2 = 1/2$) and positive

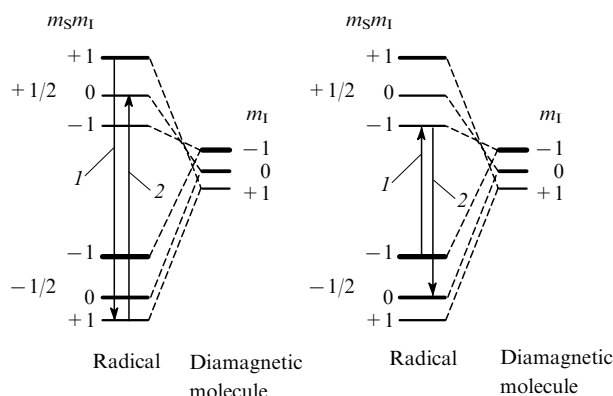


Figure 3. Schematic illustration for the mechanism of the generation of multiplet DPN of the diamagnetic products formed from short-lived radicals. The arrows show the resonance transitions induced by an RF field (1) and cross-relaxation transitions (2).

HFC constants ($A_1 = A_2$).³² Cross-relaxation occurs by a contact mechanism ($\Delta m = 0$).

Study of the dependences of DNP of stable radicals of paramagnetic ions on the temperature, solvent viscosity, and the magnetic field strength makes it possible to solve diverse problems, for example, to study the effect of the medium on the interaction of various molecules with free radicals, to study the roles of the contact and dipole interactions during relaxation, to determine the mechanisms of interaction between radicals and nuclei, etc.[‡]

1. Dynamic nuclear polarisation of neutral intermediate short-lived radicals

Grishin *et al.*¹⁹ was the first to consider the possibility of using the DNP effects for the investigation of intermediate short-lived radicals. Photolysis of benzaldehyde in CCl_4 affords the radical pairs $[\text{Ph}\dot{\text{C}}\text{H}(\text{OH}) \text{Ph}\dot{\text{C}}\text{O}]$.¹⁹ α -Hydroxybenzyl radicals are converted into the starting benzaldehyde upon hydrogen atom transfer. In strong magnetic fields (330 mT), DNP can be detected in the NMR signals of all the diamagnetic reaction products.^{19,33–35} The negative sign of DNP corresponds to a dipole mechanism of cross-relaxation in the intermediate α -hydroxybenzyl radical. In weak and medium magnetic fields (3 and 60 mT) in which the cross-relaxation efficiency is much lower, DNP is negligibly small, the predominant contribution to polarisation being made by SNP. As noted above, an RF field induces nuclear polarisation both by the DNP mechanism, due to cross-relaxation processes in free radicals, and by the SNP mechanism, due to the change in the rate of singlet–triplet transitions in radical pairs. The contributions of these mechanisms to the polarisation of the nuclei of diamagnetic products formed from short-lived radicals can be separated based on the dependence of the width of resonance lines and the SNP and DNP intensities on the RF field amplitude (B_1). For example, photolysis of benzaldehyde in CHCl_3 has been used to study the influence of the RF-field amplitude on the ratio of the SNP and DNP contributions and on the width of individual components of the spectrum.²⁰ This permitted the researchers to estimate the lifetime of the radical pairs (~ 20 ns).

The possibility of separating the contributions of DNP and SNP to the total polarisation by varying the external magnetic field, the RF-field amplitude and the lifetimes of radicals was demonstrated¹² in relation to the photolysis of benzoquinone in solutions. For semiquinoid radicals, the efficiency of cross-relaxation in 50.0 mT fields becomes substantial, and the observed DNP is comparable in magnitude with SNP. For durosemi-

quinoid radicals, cross-relaxation is due to the modulation of HFC caused by rotation of the methyl groups (*i.e.* cross-relaxation follows a contact mechanism); in this case, a positive DNP effect is observed.^{20,21,31–36}

Information on electron relaxation times in short-lived radicals and on the rate of chemical reactions can be gained by using pulsed generation of radicals and by investigating the variation of DNP intensity in the magnetic field corresponding to the maximum of the resonance line *vs.* the time delay between the laser pulse and the leading edge of the RF pulse. These experiments for the neutral radicals generated upon photolysis of benzaldehyde in chloroform were first performed by Yamakage *et al.*³⁷ The experimental results were processed by calculations in terms of the kinetic scheme for the occupancies of the radical levels with allowance for cross-relaxation, electron transitions and the chemical reaction. It was shown that the DNP kinetics actually reflect the radical kinetics and do not depend on the cross-relaxation rate, while the DNP intensity is determined by the ratio of the cross-relaxation, electron relaxation and the chemical reaction rates. The results provided grounds for concluding that the cross-relaxation rate for the α -proton of the α -hydroxybenzyl radical is one or two orders of magnitude lower than that for aromatic protons.

Cross-relaxation processes influence substantially the chemically induced dynamic electron polarisation (CIDEP) of short-lived radicals^{38–40} and, in some cases, account for the change in its sign. Thus McLauchlan *et al.*^{39,40} found the change in the CIDEP sign in the photolysis of aliphatic ketones and suggested that this is due to the cross-relaxation in the intermediate radical. Subsequently, in a theoretical study of the cross-relaxation processes, it was shown⁴¹ that CIDNP and CIDEP are related in time and their kinetics should be considered jointly. Thus, the transfer of electron polarisation to the nuclei should substantially affect the CIDNP kinetics. Experimental research on photolysis of aliphatic ketones by the time-resolved CIDNP method gave ambiguous results. Tsentalovich *et al.*^{42–46} concluded that, when analysing the kinetics of CIDNP detected during the photolysis of acetone in isopropanol and 2,4-dihydroxy-2,4-dimethylpentanone, one should take into account the contribution of the cross-relaxation mechanism. However, Fischer *et al.*⁴⁷ showed that the CIDNP kinetics can be adequately described without allowance for cross-relaxation; only two-photon processes resulting in CIDNP of some reaction products should be taken into account. In addition, CIDEP with a positive sign is observed in the photolysis of 2,4-dihydroxy-2,4-dimethylpentanone, which refutes the conclusions about generation of CIDNP by the cross-relaxation mechanism made by Salzmann.⁴⁵ The main difficulty in comparison of the results obtained by the CIDEP and CIDNP methods is that the fields used in CIDEP experiments are about 330 mT, while the operating fields of NMR spectrometers are usually in the range 3–7 T. The electron and cross-relaxation times are known to depend appreciably on the external magnetic field, while the processes of polarisation transfer are, in turn, determined by these times.

The use of the DNP method clarified the point concerning the nature of inversion of the CIDEP sign.³² A study of the DNP in reactions involving $\text{Me}_2\text{XC}\dot{\text{C}}$ radicals ($\text{X} = \text{Me}, \text{OH}, \text{D}, \text{COMe}$) demonstrated unambiguously the presence of effective scalar ($\Delta m = 0$) electron–nuclear cross-relaxation in the *tert*-butyl and 2-hydroxyprop-2-yl radicals and the absence of cross-relaxation in 2-acetyl and prop-2-yl radicals. Figure 4 shows the DNP and EPR spectra recorded in the X and L ranges for the $\text{Me}_2(\text{OH})\dot{\text{C}}$ radical, resulting from photolysis of 2,4-dihydroxy-2,4-dimethylpentanone in benzene. It can be seen that the signs of polarisation coincide and the intensity ratios of the lines in the spectra are closely similar. Comparison of the obtained results with the results of time-resolved CIDNP studies led to the conclusion that the cross-relaxation is due to the modulation of the isotropic HFC with a characteristic correlation time of $\tau_c \gg 1$ ps.

[‡] The DNP studies of stable radicals are surveyed comprehensively in Ref. 31.

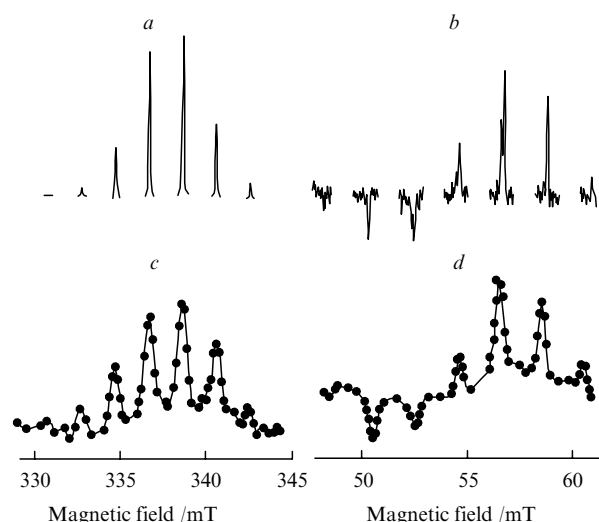
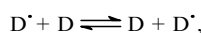


Figure 4. Spectra of 2-hydroxyprop-2-yl radical recorded in the X and L ranges by the time-resolved EPR (a, b) and DNP (c, d) methods. The resonance frequency is 10 (a, c), 1.6 (b) and 1.53 GHz (d).

2. Dynamic nuclear polarisation in radical ions

Radical-ion reactions are accompanied, in the majority of cases, by degenerate electron exchange (DEE) reactions



(D is donor, A is acceptor); therefore, the DNP in radical-ion reactions has several specific features.

In a study of the influence of an RF field on the nuclear polarisation of the products of radical-ion reactions in weak magnetic fields, a pronounced DNP effect was found.⁴⁸ Further studies demonstrated^{22, 49} that this effect is observed in the presence of DEE provided that the magnitude of the external magnetic field is comparable with the HFC constant of the radical ion.

Two different approaches have been proposed for quantitative description of DNP under the conditions of DEE in weak magnetic fields.^{22, 49} One approach is based on numerical solution of the Liouville equation for the spin density matrix of the radical with allowance for the spin dynamics in a weak magnetic field and the DEE process, while the other approach includes solution of the Bloch phenomenological equations with allowance for the relaxation times T_1^e , T_2^e

$$\frac{1}{T_1^e} = 2A^2\tau_e \frac{1}{1 + \omega_0^2\tau_e^2};$$

$$\frac{1}{T_2^e} = A^2\tau_e \left(1 + \frac{1}{1 + \omega_0^2\tau_e^2} \right),$$

where $A^2 = \frac{1}{3} \sum_i I_i(I_i + 1)A_i^2$ is the second moment of the EPR

spectrum of the radical ion for nuclei with spins I_i and HFC constants A_i , τ_e is the DEE time, and ω_0 is the Larmor frequency of electron spins.

The former approach is applicable to any DEE rates, while the latter one is suitable only for high exchange rates ($A^2\tau_e^2 \ll 1$). The main advantages of the latter model include its simplicity and the possibility of using it to study radicals with complex EPR spectra. Comparison of the DNP spectra calculated in terms of these two models showed that at high rates of electron exchange, the spectral patterns are identical; in this case, the use of the phenomenological approach is quite justified. Note that both models take into

account only processes which occur in radical ions, the influence of the RF field on the radical pairs being ignored. Of course, this assumption is rather simplified because the RF field induces singlet–triplet transitions in the radical ion pairs and, thus, it can, in principle, induce CIDEP.⁵⁰ The line shape in the DNP spectrum in the absence of CIDEP was compared to that obtained with the assumption that CIDEP does not depend on the fields B_1 and B_0 . It was shown that the distinctions become significant in the case of DEE and large B_1 values, *i.e.* in those cases where the spectrum width becomes comparable with the field magnitude B_0 .

The DNP effects have also been studied in the photolysis of anthracene with dimethyl- or diethyl-aniline and in the photosensitised *cis*–*trans* isomerisation of fumaronitrile in the presence of naphthalenes.^{22, 24, 49, 51} The researchers studied the influence of the electron exchange rate and the amplitude of the RF field on the pattern of DNP spectra; the results were in good agreement with theoretical predictions. The dependence of the half-width of the spectrum on the reciprocal concentration of diamagnetic molecules participating in the charge exchange was used to determine the rate constants for the electron exchange of the dimethyl- and diethyl-aniline radical cations.

The sign of CIDEP is known to be determined by the multiplicity of the radical pair and by the sign of exchange interaction.⁵² Upon the change in multiplicity, the sign of CIDEP and, hence, the sign of DNP should be reversed. This was observed,^{25, 51} for example, in the photosensitised isomerisation of fumaronitrile in 1,4-dimethoxynaphthalene. The triplet state of the excited 1,4-dimethoxynaphthalene molecule is lower in energy than the radical-ion pair; therefore, by changing the concentration of fumaronitrile, one can change the multiplicity of the radical pair.⁵³

The measurement of the DEE rate constants can be markedly simplified by proceeding from the dependence of the DNP kinetics on the concentration of the diamagnetic product. This method has advantages over investigation of the concentration dependence of the half-width of the DNP spectra because the half-width of the spectra depends appreciably on the amplitude of the RF field B_1 , whereas the DNP kinetics do not. For the first-order reaction of radical decay, an analytical solution was found; for the second-order reaction, a numerical solution was obtained.⁴⁹ It was shown that the DNP kinetics are determined by the time of electron exchange τ_e , the time of electron relaxation T_1^e and the lifetime of radical ions τ_i . For high concentrations of diamagnetic molecules involved in DEE, the kinetics are described by an exponential function with a decay parameter equal to T_1^e . Figure 5 shows the experimental curves for the DNP kinetics of the photolysis of fumaronitrile with perdeuterated naphthalene. Any curve for $\tau_i > 100$ ns can be described by the exponential function $\exp(-k_{\text{obs}}\tau_i)$, where k_{obs} is the observed rate constant for the exponential decay. The initial pattern of the curve presented in Fig. 5b is due to the time for generation of radical ions. At high concentrations of molecules participating in charge exchange, *i.e.* at low times of DEE, the condition $T_1^e \ll \tau_i$ holds, T_1^e and the experimental dependences of k_{obs} on the concentration of fumaronitrile being adequately described by the formula

$$k_{\text{obs}} \simeq \frac{1}{T_1^e} = \frac{2A^2\tau_e}{1 + \omega_0^2\tau_e^2}.$$

The rate constant for DEE k_e is equal to $(4.52 \pm 0.23) \times 10^9$ litre mol^{−1} s^{−1} and is close to the value estimated from the concentration dependence of the spectra.

In a series of studies,^{25, 54, 55} the DNP method together with time-resolved EPR were employed to identify the radical species resulting from photolysis of heteroaromatic azines in the presence of dimethylaniline in polar solvents. In the DNP study of all the compounds, except for phenazine, the recorded spectra of the dimethylaniline radical cation were narrowed down due to the DEE reaction. This provided grounds for conclusion that the radical-ion pathway contributes to the formation of the compounds under consideration.

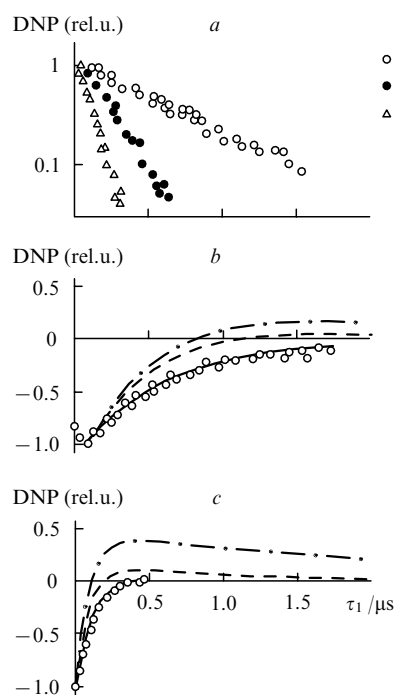


Figure 5. Time dependences of DNP obtained for the photolysis of naphthalene- d_8 ($c = 5 \times 10^{-4}$ mol litre $^{-1}$) with fumaronitrile in CD_3CN at different DEE rates. Fumaronitrile concentration (mol litre $^{-1}$): (a) 5×10^{-3} (1), 2×10^{-2} (2), 4×10^{-2} (3); (b) 5×10^{-3} ; (c) 4×10^{-2} . The absolute magnitudes of DNP are plotted on a logarithmic scale (a). The continuous lines (b, c) correspond to the decay of radical ions by an exponential law, dashed lines show the second-order decay of radical ions and describe the contributions of the minor geminate (dashed line) and diffusion polarisations (chain line).

3. Electron–nuclei transitions in short-lived radicals in weak magnetic fields

The influence of an RF field on the nuclear polarisation of diamagnetic products of radical reactions in weak magnetic fields, whose magnitudes are comparable with the HFC constants of radicals, possesses several specific features: the intrinsic wave functions of radicals are no longer the products of the electronic and nuclear wave functions, and the resonance transitions are not purely electronic or nuclear transitions. Therefore, all transitions in these fields involve both the nuclear and the electronic spins. Therefore, the use of relatively low RF-field amplitudes results in substantial changes in the occupancy of the electron–nuclear levels. This effect was called NMR detected electron–nuclear transitions in short-lived radicals (NMR ENR).^{56, 57}

The diagram of the electron–nuclear spin levels of a radical with one magnetic nucleus with the spin 1/2 is shown in Fig. 6. In a weak magnetic field, the probabilities (P) of transitions $n_1 \rightleftharpoons n_2$ and $n_3 \rightleftharpoons n_4$ on exposure to a resonance field are proportional to the expression

$$P_{n_i \rightleftharpoons n_j} \sim |\langle \Psi_{n_i} | \hat{B}_{1x} (\hat{S}_x + \hat{I}_x) | \Psi_{n_j} \rangle|^2 = B_1^2 [\gamma_e \beta_e^2 + c_2^2 (\gamma_n \beta_n)^2],$$

where n_i, n_j correspond in pairs to n_1, n_2 and n_3, n_4 ; Ψ_{n_i} are the wave functions of the $n_{i,j}$ states; the coefficients c_1 and c_2 are determined by the relationship between the HFC constant and the B_0 value. When the magnetic field changes, the coefficients c_1^2 and c_2^2 change from 1 and 0, respectively, in strong magnetic fields (where $n_1 \rightleftharpoons n_2$ and $n_3 \rightleftharpoons n_4$ are purely nuclear transitions) to 0.5 and 0.5, respectively, in the zero magnetic field in which these transitions involve changes in the projections of both electron and nuclear spins. In a strong magnetic field ($c_1 = 1, c_2 = 0$), sub-

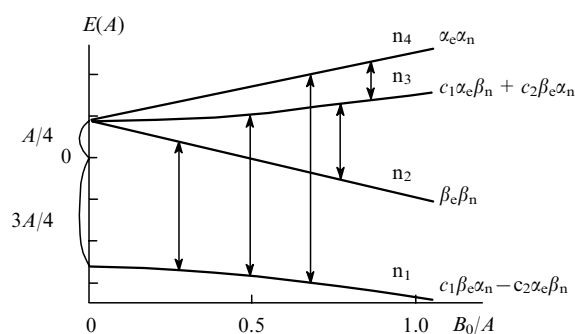


Figure 6. Scheme of the energy levels of a radical with one magnetic nucleus and the spin 1/2 in a magnetic field. The arrows show all the transitions allowed in a weak field.

stantial amplitudes of the radio-frequency field are required to saturate these transitions in short-lived radicals

$$B_1 \approx \frac{1}{\gamma_n \tau^*},$$

where

$$\frac{1}{\tau^*} = \frac{1}{T_1^n} + \frac{1}{\tau_1} + \frac{1}{T_{cr}},$$

T_1^n is the time of nuclear relaxation of the radical, τ_1 is the lifetime of the radicals and T_{cr} is the time of electron–nuclear cross-relaxation. With the real values $T_1^n \approx 10^{-4}$ s, $\tau_1 \approx 10^{-5} - 10^{-6}$ s, $T_{cr} \approx 10^{-5}$ s, we have $B_1 \approx 1 - 10$ mT. In weak magnetic fields ($c_1^2 \approx c_2^2$), the probability of transitions is high even for much smaller amplitudes of the radio-frequency field

$$B_1 \sim \frac{1}{c_1 \gamma_e \tau^*},$$

where

$$\frac{1}{\tau^*} = \frac{1}{T_1^e} + \frac{1}{\tau_1} + \frac{1}{T_{cr}},$$

T_1^e is the time of electron relaxation of the radical. Thus, in weak magnetic fields, the probability of transitions is high when radio-frequency fields of about 10^{-2} mT are used.

In radical reactions, the occupancies of electron–nuclear sublevels of radicals are usually non-equilibrated due to CIDNP. It is evident that saturation of transitions would result in equalisation of the occupancies and in a substantial change in the nuclear polarisation of the diamagnetic products. In weak magnetic fields, a radio-frequency field acting parallel to an external magnetic field induces the $n_1 \rightleftharpoons n_3$ transition (see Fig. 6), forbidden in strong magnetic fields. The probability of this transition is proportional to the value $(c_1 c_2 \gamma_e B_1)^2$.

Theoretical description of the NMR ENR effect was made using the numerical solution of the Liouville equation for the spin density matrix of the radical with allowance for electron and nuclear relaxation. Theoretical analysis of the main features of this effect showed that its magnitude is determined by several factors, namely, by the amplitude of the applied radio-frequency field, the coefficients c_1 and c_2 , the lifetime of radicals in solution and by the occupancy of the corresponding electron–nuclear levels (Fig. 7). It can be seen that at relatively small amplitudes of the radio-frequency field, the magnitude of this effect does not depend on the type of the transition excited, while at large amplitudes, it does depend on the type of transition. Thus, by comparing the polarisation intensities corresponding to different transitions in the same magnetic field, one can calculate the occupancies of all the electron–nuclear spin levels of free radicals; analysis of the line shape provides information concerning the

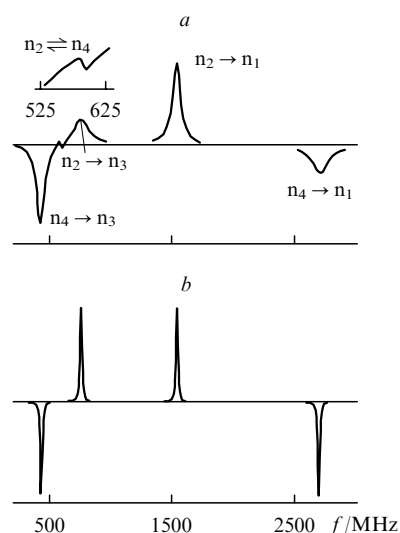


Figure 7. Theoretical NMR ENR spectra. Initial occupancies of the levels $n_1 = 0$, $n_2 = 1/2$, $n_3 = 0$, $n_4 = 1/2$. The multiplet CIDNP arises in a 42 mT magnetic field, $\tau_1 \ll T_{1,2}$, $A = 70$ mT, the amplitude of the applied radio-frequency field B_1 (mT): (a) 3, (b) 0.001.

relaxation times of radicals in a weak magnetic field and on their lifetimes.

Ananchenko *et al.*^{56–58} were the first to carry out experiments on the study of the electron–nuclear transitions in phosphonyl radicals resulting from photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide and dimethyl 2,4,6-trimethylbenzoylphosphonic acid. Figures 8 and 9 present the NMR ENR spectra recorded upon photolysis of 2,4,6-(trimethylbenzoyl)diphenylphosphine oxide (B_1 is parallel to B_0 , Fig. 8) and dimethyl

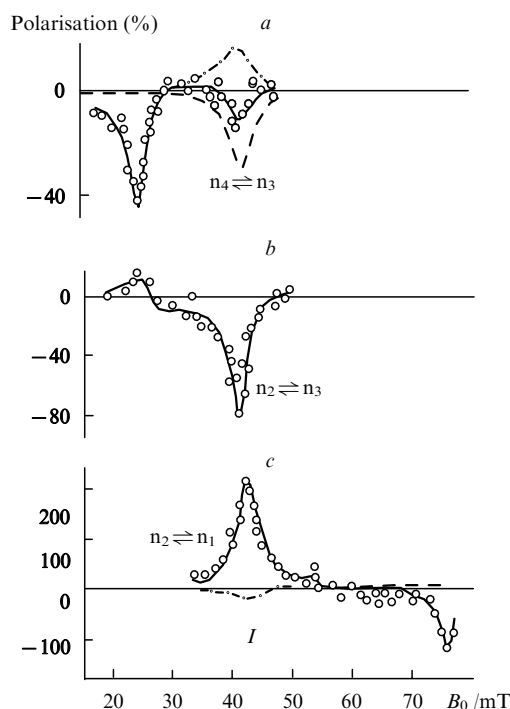


Figure 8. NMR ENR spectra of the diphenylphosphinyl radical $\text{Ph}_2(\text{O})\text{P}^\bullet$. RF-field frequency ν (MHz): (a) 431, (b) 750, (c) 1530; RF-field amplitude B_1 (mT): (a, c) 1.1, (b) 1.2. Continuous lines are the simulated spectra constructed as the sum of the SNP contributions (chain line) and the theoretical NMR ENR spectra (dashed line).

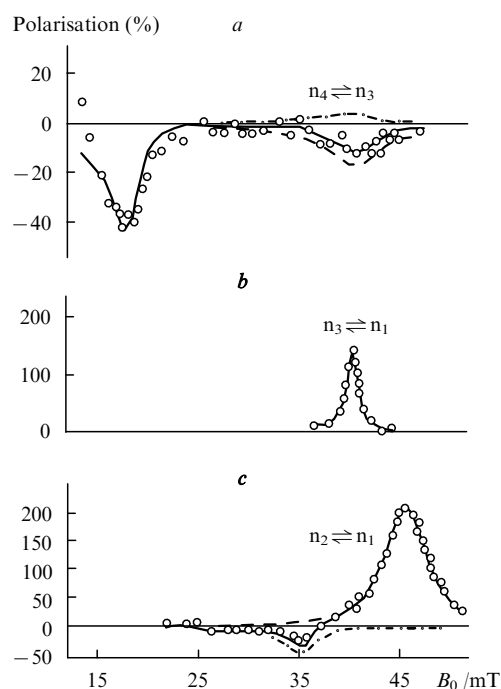


Figure 9. NMR ENR spectra of the dimethylphosphonyl radical $(\text{MeO})_2(\text{O})\text{P}^\bullet$. RF-field frequency ν (MHz): (a) 315, (b) 1530, (c) 694; RF-field amplitude B_1 (mT): (a) 1.2, (b) 0.7, (c) 0.9. For the designation of lines, see Fig. 8.

2,4,6-trimethylbenzoylphosphonate in dioxane (B_1 is perpendicular to B_0 , Fig. 9). Polarisation was measured in percent of CIDNP for $B_0 = 42$ mT. It can be seen that the intensity of the $n_1 \rightleftharpoons n_2$ and $n_1 \rightleftharpoons n_3$ transitions exceeds the intensity of the $n_4 \rightleftharpoons n_3$ transitions by a large factor. Based on analysis of the intensities and the signs of resonance lines in the spectrum, it was shown that the initial occupancy of the level n_1 is negligibly small compared to that of the levels n_2 , n_3 or n_4 . Thus, it can be concluded that in weak magnetic fields, the magnitudes of which are lower than the HFC constants of radicals, intense electron polarisation should be observed. It is noteworthy that the results are in good agreement with the conclusions based on analysis of the field dependences of CIDNP for radical pairs with large HFC constants.^{59, 60}

IV. Stimulated nuclear polarisation

Stimulated nuclear polarisation is a phenomenon tightly related to other magnetic and spin effects in radical reactions, in particular, to the chemically induced dynamic nuclear polarisation. The CIDNP method does not bear direct quantitative information about the magnetic-resonance parameters of radical pairs; therefore, it should be combined with other methods such as EPR, optical spectroscopy, *etc.* For example, the use of time-resolved CIDNP, first proposed and implemented by Closs *et al.*,⁶¹ provides quantitative information on the kinetics of the intermediate radical species, the lifetimes of triplet molecules, *etc.*^{62–64}

The SNP method is a combination of CIDNP with the RYDMR principles,^{1–10, 65, 66} based on the selective influence of a variable field on the probability of recombination of separate sub-ensembles of radical pairs. The influence of an RF field on the yield of the reaction products is detected from the change of parameters of the system under study (for example, the resonance photoconductivity of organic semiconductors, the intensity of the recombination fluorescence, the optical absorption of the products, the EPR spectra of stable radicals,⁶⁷ *etc.*).

We shall consider the mechanism of SNP in relation to a radical pair with one magnetic nucleus in strong magnetic fields. Let us assume that the pair has formed in the triplet state and

recombination from the triplet state is forbidden. In the case of strong magnetic fields, the S and T_0 states are degenerate and, therefore, transitions from the non-reactive T_0 state to the reactive S state occur efficiently due to hyperfine coupling. However, transitions from the T_- and T_+ states to the S state are suppressed due to the great energy gap between these states. The CIDNP effect is known to be based on the fact that the probabilities of the S–T transitions are different for radical pairs with different orientations of the nuclear spin. Let the g -factors of the radicals be equal. In this case, the CIDNP effect for a radical pair with one magnetic nucleus is equal to zero. The resonance RF field mixes the T_0 state of the radical pair with the T_- and T_+ states, which accelerates the S–T conversion at small amplitudes of the RF field ($\omega_1 < |\Delta\omega|$) and decelerates it at great amplitudes ($\omega_1 > |\Delta\omega|$). [Here, ω_1 is the amplitude of the RF field, $\Delta\omega = \omega_\alpha - \omega_0 = \omega_0 - \omega_\beta$ is the difference between the resonance frequencies of the radicals R^1 and R^2 (partners of the $R^{1*}R^2$ radical pairs), R^1 contains the magnetic nucleus ($\omega_\alpha, \omega_\beta$) and R^2 contains no nuclei with a non-zero HFC constant (ω_0).] We assume that $\omega_1 < |\Delta\omega|$. If the resonance-field frequency is equal to the resonance frequency ω_α of electron transitions in the radical R^1 with α -orientation of the nuclear spins, the acceleration of S–T transitions would involve only the sub-ensemble of radical pairs with this spin orientation and the products of recombination of radical pairs would mainly contain nuclei with the α -projection of spins. This would result in enhanced absorption in the NMR line of in-cage products. The nuclei of the escape products of the recombination of the radical pair would be mainly characterised by the β -projection of spins and the corresponding line in the NMR spectrum would be an emission line (Fig. 10). If the frequency of the RF field is equal to the ω_β frequency of the electron transitions in the R^1 radical with the β -orientation of nuclear spins, emission would be observed in the NMR lines of the in-cage products and absorption would be observed in the spectra of escape products. The effect of the RF field on the resonance frequency of the R^2 radical (ω_0) will induce acceleration of the S–T conversion with the same efficiency for both sub-ensembles of radical pairs and, hence, will not change the nuclear polar-

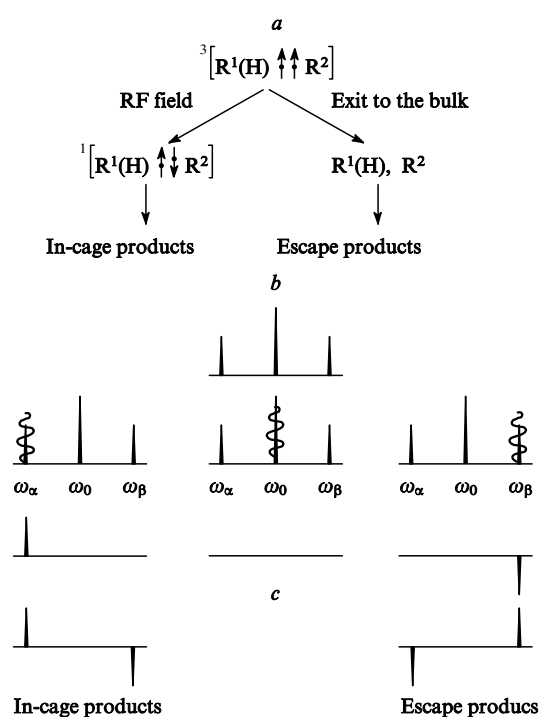


Figure 10. Scheme for the generation of SNP for a radical pair with one magnetic nucleus (a) and its EPR (b) and SNP (c) spectra.

isation of the products. Thus, the positions of the resonance lines in the SNP spectrum correspond to the resonance frequencies in the EPR spectrum of the radical pair, and the signs of the resonance lines are determined by the signs of the HFC constants and by the pathways to diamagnetic products the NMR spectrum of which is used to detect the SNP.

In the case where $\omega_1 > |\Delta\omega|$, i.e. under spin-locking conditions, the RF field retards the S–T conversion and, hence, the signs of SNP would be opposite to those observed in the case described above. On the basis of these considerations, Mikhailov *et al.*⁶⁸ formulated the rule for determining the sign of polarisation of the products for the case of net SNP

$$\Gamma = \mu\epsilon\psi\eta A_k,$$

where $\Gamma > 0$ corresponds to the positive (absorption) and $\Gamma < 0$, to the negative SNP effect (emission), $\mu = 1$ or -1 for a triplet or a singlet radical pair; $\epsilon = 1$ or -1 for the in-cage or escape product; $\psi = 1$ or -1 for low- or high-field component of the HFC spectrum of the chosen nucleus; $\eta = 1$ for $\omega_1 < |\Delta\omega|$ and $\eta = -1$ for $\omega_1 > |\Delta\omega|$, A_k is the isotropic HFC constant at the k -th nucleus polarisation of which is considered.

For radical pairs with any number of magnetic nuclei, the SNP spectrum is a superposition of the spectra of separate sub-ensembles of radical pairs with fixed configurations of nuclear spins. In a real situation when the spin dynamics of radical pairs are overlapped by the molecular motion of radicals, the spectral lines have a finite width and, in the general case, for several nuclei with different HFC constants, the SNP spectral pattern is markedly complicated. Therefore, to analyse the experimental SNP spectra, one should compare them with the theoretical spectra.

Exchange interaction markedly influences the pattern of the SNP spectra. We shall consider this influence qualitatively in relation to a biradical with one magnetic nucleus (Fig. 11 a,b). The relative positions of the energy levels are determined by the ratio of the HFC constants A , the effective exchange interaction J_0 and the external magnetic field B_0 . The effects of nuclear polarisation, both chemically induced and stimulated, depend substantially on the ratio of the intersystem crossing rates (K_{S-T_0} , K_{S-T_-}). In the case where the average exchange interaction $\gamma_e B_0 < 2|J_0|$ (Fig. 11 a), the rate of intersystem crossing via the S– T_- channel is higher than that via other channels ($K_{S-T_-} > K_{S-T_0}$, K_{S-T_+}); therefore, the occupancy of the T_-^z state is lower than those of the T_+^z or T_0^z states. Radio frequency pumps the T_-^z level and thus increases the number of radical pairs recombining upon $T_-^z \rightarrow S^0$ transitions. As a consequence, the products of recombination become enriched in the nuclei with the β -projection of nuclear spins. The SNP spectrum of radical pairs is an emission line. Otherwise, $\gamma_e B_0 > 2|J_0|$ ($K_{S-T_0} > K_{S-T_-}$, K_{S-T_+}) (Fig. 11 b) and the occupancy of the T_0^z state is lower than that of the T_-^z or T_+^z states. In this case, the number of radical pairs recombining via the S– T_0 channel of intersystem crossing increases under the action of the RF field. The SNP spectral pattern is normal — the signs of polarisation of the spectral lines depend on the signs of the projection of the nuclear spins, the exchange interaction being manifested as a change in the line splitting in the spectrum. Thus,

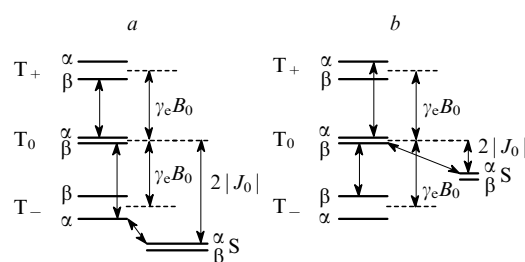


Figure 11. Diagram of the electron levels of a biradical with one magnetic nucleus for strong (a) and weak (b) exchange interaction.

the magnitude of exchange interaction can be judged both from the pattern of the S–T₀ or S–T_– type spectrum and from the splitting in the S–T₀ type SNP spectrum. Apart from the exchange interaction, splitting in the SNP spectra is influenced by spin-selective decay of radical pairs, which can diminish splitting even in the absence of exchange interaction.⁶⁹ It was shown^{69,70} that exchange interaction, electron relaxation and fast decay of the singlet state are factors influencing the splitting of lines in the SNP spectra because they all result in dephasing of the singlet–triplet transitions.

Theoretical description of the SNP effects has been the object of a number of studies^{69–81} in which various approaches were employed. Thus Mikhailov *et al.*⁶⁸ developed a theory of SNP for reactions of neutral radicals with isotropic reactivity in strong magnetic fields based on the mathematical apparatus used traditionally to study the geminate recombination of radicals with allowance for the S–T₀ transitions in radical pairs. The SNP effects were calculated in this study by summing the contributions to recombination of all the radical re-encounters.⁸² This method is based on the assumption that the spin dynamics in radical pairs and relative molecular motion of radicals in solution are completely separate and implies the use of numerical calculations. However, numerical analysis of the SNP effects in systems with many magnetic nuclei is highly time-consuming. Analytical expressions have been obtained^{72,83} for the calculation of the probability of recombination of radical pairs with a specified configuration of nuclear spins and of the SNP effects on the assumption of low efficiency of singlet–triplet transitions in radical pairs.

The effects of various parameters on the line intensity and the pattern of the SNP spectrum have been studied theoretically.⁶⁸ It was shown that the intensity and the sign of SNP as well as the spectral pattern depend substantially on many molecular-kinetic and magnetic-resonance parameters of the radical pair, solvent viscosity, reactivity of radicals, the occurrence of reactions of the radicals with acceptors, the amplitude and the frequency of a microwave field, the HFC constants and *g*-factors of radicals. Therefore, detailed interpretation of experimental data can only be performed resorting to calculations of the SNP effects.

Osintsev *et al.*⁸⁴ used the kinematic approach to derive the analytical expressions for calculating the SNP effects of radical pairs with one HFC constant in arbitrary magnetic fields. In another study,⁷³ these researchers analysed the line profile in the SNP spectra in weak magnetic fields, comparable with the HFC constant, for different RF-field amplitudes. It was shown that in weak fields, additional lines which are missing in strong fields appear in the spectrum.

The effect of a powerful RF field during recording of the SNP spectra in weak magnetic fields gives rise to new resonance characteristics in the spin dynamics of radical pairs, which are multi-quantum resonances from the standpoint of quantum theory.⁷⁴ Experimentally, this shows itself as the appearance of signals in the SNP spectra in the Zeeman fields *B*₀ approximately divisible by the field of the main resonance.²⁵ The kinematic approximation has also been used successfully⁷³ to design the theory of multi-quantum resonances under the conditions of SNP.

Characteristic features of the SNP spectra for spin-correlated radical pairs in strong magnetic fields have been considered taking a two-position model as an example.⁸¹ It was found that narrow lines the nature of which is due to the degeneracy of two electron transition frequencies appear in the SNP spectra under definite conditions. From the width of these lines, the lifetime of spin-correlated radical pairs can be determined. Note that similar features are characteristic of the spectra of radical pairs measured using the optically detected electron paramagnetic resonance (OD EPR) technique.⁸⁵

The SNP effects in systems with non-zero exchange interaction depending on the distance between the radical sites (short-lived biradicals,⁶⁹ radical pairs in micelles^{75–78}) can be described

using an approach based on the numerical solution of the stochastic Liouville equation.

1. Stimulated nuclear polarisation of radical pairs in homogeneous solutions

The SNP effects were first observed experimentally for recombination of the biradicals formed upon photolysis of cyclododecane.⁸⁶ Subsequently, it has been shown in relation to the photolysis of benzoyl peroxide in various solvents⁸⁷ that recombination of radicals in the liquid phase proceeding *via* the formation of radical pairs consisting of the phenyl and phenacyl radicals [Ph[•]OC(O)Ph] is accompanied by substantial polarisation. Bagryanskaya *et al.*⁸⁷ carried out experiments in weak magnetic fields (*B*₀ = ~ 3.0 mT, *ν* = 94.5 MHz), the magnitudes of which are comparable with the HFC constants in the phenyl radical. The pattern of the SNP spectrum was complex, which substantially hampered interpretation of the data obtained, especially for *B*₁ ≈ *A*. Subsequently, the main regularities of SNP have been investigated in the photolysis of *p*-benzoquinone and duroquinone in CD₃CN, CDCl₃ and CD₃OD in weak and strong magnetic fields.^{12,20,21,34,88} Photolysis of benzoquinone in CD₃CN has been used as an example to study⁸⁶ the effect of spin locking, which was then employed to estimate the amplitude of the RF field when working in a high-frequency resonator. By comparing the dependences of SNP on the amplitude of the radio-frequency field in weak magnetic fields in the case of low pumping frequency (100 MHz, when measurements of the *B*₁ value are rather simple) and in strong magnetic fields in the case of high pumping frequency (1.6 GHz), one can determine the amplitude *B*₁ in the resonator for the high-frequency case. Multi-quantum resonances were detected experimentally in the high-field region of the SNP spectra measured at great RF field amplitudes (*B*₁ ≫ *A*).²⁵

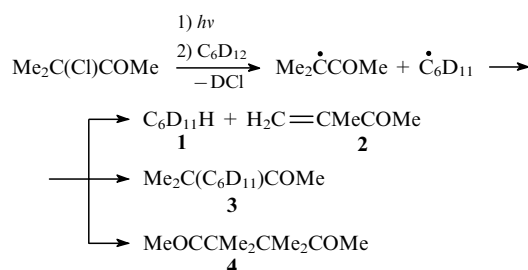
As noted above, the method of SNP permits identification of intermediate short-lived species (radical and radical-ion pairs) and also provides information on the pathways of formation of the reaction products. For example, SNP has been used⁸⁹ to study elementary steps in the photolysis of anthraquinone (AQ) with triethylamine in solvents with different polarities. For the reaction carried out in polar solvents (CD₃CN, CD₃OD), the spectrum of triethylamine radical cation was measured using the NMR line of the triethylamine CH₂ group. Based on the sign of the spectrum, it was concluded that triethylamine is an in-cage product of recombination of the radical-ion pair {[AQ]^{–•}··⁺[Et₃N]}[•]. For the photolysis of triethylamine and anthraquinone in CD₃OD, the SNP spectrum was measured based on the NMR signal of the proton of the hydroxy group in CD₃OH. This spectrum differed from the SNP spectrum recorded using the signal of the triethylamine CH₂ group only by the sign; hence, it corresponds to an escape product of transformation of the triethylamine radical cation. This fact indicates that the hydroxyl proton of the alcohol has come from the CH₂ group of the triethylamine escape radical cation. Thus, the authors concluded that the reaction takes place between hydroxyalkyl and aminoalkyl radicals. In non-polar solvents, in particular, in benzene, the SNP spectrum corresponds to the EPR spectrum of the aminoalkyl radical MeCH₂NEt. In medium-polarity solvents (cyclohexane and isopropanol), both pathways are effective (the radical-ion and radical pathways).

It should be borne in mind that signals in the SNP spectra can differ substantially for continuous and pulse photolysis modes.^{28,90} For example, the intensity of signals recorded during pulse laser photolysis of benzoquinone and benzaldehyde decreases by a factor of dozens when a mercury light is used as a continuous source of light. The signal intensity in the SNP spectra does not change if the radicals decay in a first-order reaction, for example, in the photolysis of benzoyl peroxide, cyclic ketones, *etc.* In the steady-state photolysis, the lifetime of radicals normally exceeds the time of nuclear relaxation of the intermediate radicals (10^{–4} s), the observed polarisation being due to the contribution of the polarisation of the in-cage recombination products. In the

case of pulse generation of radicals, the opposite situation is observed, *i.e.* the lifetime of radicals is usually shorter than the nuclear relaxation time. Hence, the total polarisation of diamagnetic products formed both in the cage and as a result of radical recombination in the bulk markedly decreases or disappears.

In a study of laser photolysis of *p*-benzoquinone in methanol by SNP, it has been found^{25,91} that cyclohexadienyl type radicals with methoxy- or hydroxymethyl groups participate in the reaction. The SNP spectra based on the signals present in the NMR spectra of benzoquinone, hydroquinone and the alcohol (the hydroxyl-proton signal) differ appreciably from the SNP spectra of radical pairs of semiquinoid radicals measured for continuous photolysis under the same conditions. The distance between the terminal lines in the spectrum (4.5 mT) indicates that the reaction involves radicals with the high HFC constants of the ring protons. Comparison of experimental SNP spectra with those calculated for several assumed radical species with allowance for HFC constants (calculated by the MNDO method) made it possible to establish the structure of the intermediate radical.

Figure 12 *a, b* shows the NMR and SNP spectra recorded for the photolysis of 2-chloro-2-methylbutan-3-one in C₆D₁₂.³²



Stimulated nuclear polarisation is observed for all diamagnetic products 1–4. The experimental spectra of in-cage products are in good agreement with the spectra calculated for the [Me₂(CO-Me)C[•]·C₆D₁₁] radical pair. To attain agreement between the theoretical and experimental SNP spectra of escape products,

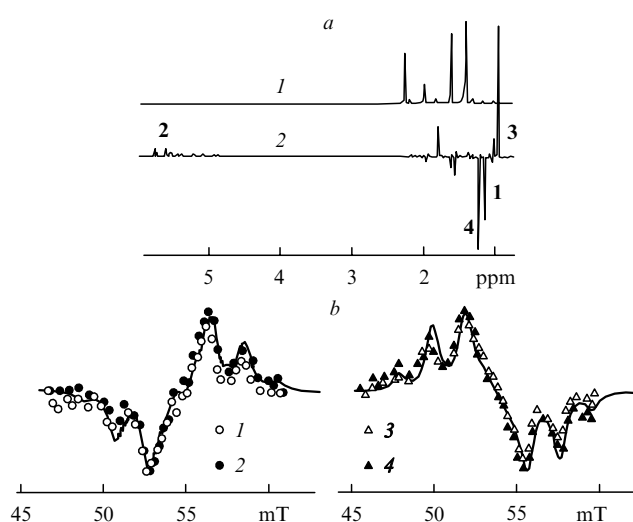


Figure 12. NMR spectra recorded for the photolysis of 2-methyl-2-chlorobutan-3-one in C₆D₁₂ (*a*) [(1) spectrum in the dark, (2) CIDNP spectrum] and experimental and simulated SNP spectra for reaction products (*b*); (1) product 1, (2) product 2, (3) product 4, (4) product 3. The continuous lines are simulated spectra. (1, 2) with allowance for the contributions to SNP of the escape products of the geminate radical pair [Me₂(COMe)C[•]·C₆D₁₁] and in-cage products of the diffusion radical pair [Me₂(COMe)C[•]·C(COMe)Me₂]; (3, 4) calculations of the SNP of the in-cage products from the geminate radical pair [Me₂(COMe)C[•]·C₆D₁₁].

contributions of both radical pairs, [Me₂(COMe)C[•]·C₆D₁₁] and [Me₂(COMe)C[•]·C(COMe)Me₂], should be taken into account.

The influence of the DEE rate on the pattern of SNP spectra has been studied.⁴⁸ It was shown that, since DEE results in frequency exchange between the components of the spectrum with opposite polarisation signs, the narrowing of lines is accompanied by a decrease in their intensities; in the limit, the lines disappear.

The influence of DEE on the SNP effect has been studied in detail both experimentally and theoretically.⁹² The researchers used two approaches to the theoretical description of the SNP spectra with allowance for DEE. In the former case, the spectra were calculated using the theory of uncorrelated frequency migration for a radical pair with two magnetic nuclei. In the latter case, for a weak RF field ($B_1 \ll A$), a two-position model was proposed. In the case of low DEE rates ($A\tau_e \gg 1$, where τ_e is the time of DEE, $\tau_e = 1/k_e[A]$ (or $[D]$), $[A]$ or $[D]$ is the concentration of the acceptor or the donor participating in the DEE reaction), this model provides an analytical expression describing the variation of the SNP amplitude *vs.* the exchange time τ_e . Photo-induced isomerisation of fumaronitrile in the presence of deuterated naphthalene in acetonitrile was chosen as the model reaction for experimental investigations. Figure 13 shows the SNP spectra of radical pairs resulting from photolysis of fumaronitrile with naphthalene over broad ranges of DEE rates and RF-field amplitudes. At low fumaronitrile concentrations when the influence of DEE is negligibly small, the SNP spectra resemble the spectra based on calculations for neutral radical pairs without

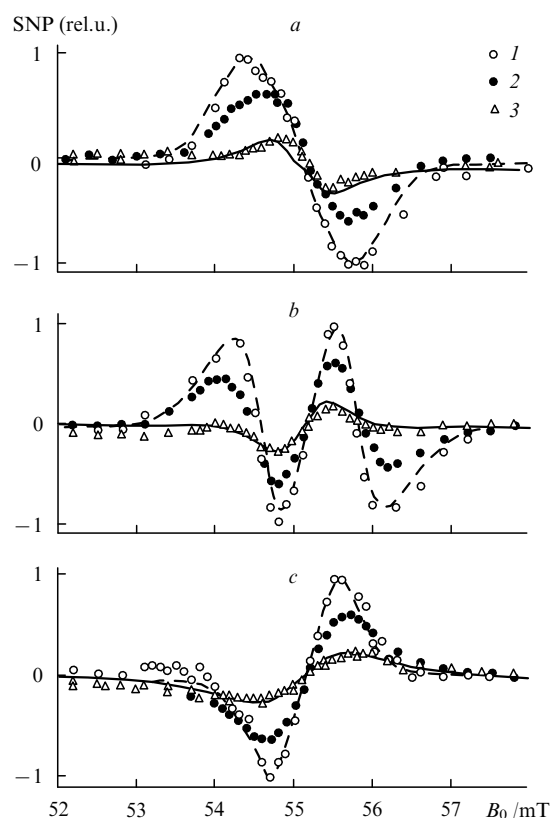


Figure 13. SNP spectra recorded for the photolysis of naphthalene-d₈ (2×10^{-3} mol litre⁻¹) with fumaronitrile and detected from the NMR signal of the fumaronitrile protons. Fumaronitrile concentration (mol litre⁻¹): (1) 10^{-3} , (2) 10^{-2} , (3) 5×10^{-2} . RF-field amplitudes (mT): (*a*) 0.25, (*b*) 0.67, (*c*) 1.2. The dashed lines correspond to the spectra calculated with allowance for all the HFC constants using the theory of SNP for neutral radical pairs without DEE. The continuous lines are the spectra calculated using the theory of uncorrelated frequency migration for a radical pair with two magnetic nuclei.

allowance for charge exchange. The calculation was carried out taking into account all the HFC constants in radical pairs in terms of the theory of SNP in strong magnetic fields. It can be seen from Fig. 13 that the pattern of the SNP spectra is extremely sensitive to the RF-field amplitude. As the concentration of fumaronitrile increases, SNP sharply decreases; line splitting in the spectra also decreases. To measure the rate constant for DEE in radical-ion reactions by comparison of the theoretical and experimental SNP spectral patterns, the dependence of the SNP intensity on the exchange time τ_e at low RF-field amplitudes in the absence of fast trapping of radical ions was used.

The SNP method was utilised to study the photoinduced electron transfer from quadricyclanes to tetrafluorobenzoquinone. It was shown⁹³ that the radical-ion pair in this reaction incorporates the quadricyclane radical cation. Isomerisation of quadricyclane into norbornadiene takes place in the free radical ion rather than in the step of formation of the radical-ion pair.

The majority of researchers studied reactions in homogeneous solutions by ^1H NMR spectroscopy. However, detection of SNP using other nuclei (^{13}C , ^{31}P , ^{19}F , etc.) appears quite promising. Figure 14 presents the ^{31}P SNP spectrum of the radical pair formed in the photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide. Splitting in the spectrum corresponds to the HFC constant at the phosphorus nucleus. A specific feature of SNP at the ^{31}P nuclei is large HFC constants comparable with the magnitude of the external magnetic field. Therefore, calculations cannot be carried out using the strong magnetic field approximation. In addition, for radical pairs with large HFC constants, contributions of S–T₋ transitions occurring in the area of intersection of terms should be taken into account.^{59, 60}

The potential and advantages of the time-resolved SNP method were verified experimentally²⁸ taking photolysis of benzoyl peroxide (in CD_3OD or CD_3CN) as an example. It was shown that the delay (τ) between the laser pulse and the RF pulse inverts the observed SNP spectrum. A study of the dependence of SNP on τ in different magnetic fields for different resonance lines demonstrated that the inversion of the spectrum takes place at $\tau > 50$ ns, and subsequently the spectral pattern changes only slightly. Apparently, the spectrum corresponds to the $[\text{Ph}^\bullet\text{Ph}]$ and $[\text{Ph}^\bullet\text{CD}_2\text{OD}]$ pairs.

Osintsev *et al.*⁸⁴ have considered theoretically the problem of the line shape in the SNP spectra recorded in time-resolved experiments and the dependence of SNP on the character of motion of the partners of radical pairs. From the theoretical standpoint, consideration of these processes is reduced to the

calculation of the probability of recombination of geminate radical pairs. (The theory of recombination of radical pairs with a Hamiltonian changing abruptly with time has been formulated.^{94, 95}) It was shown⁸⁴ that the width of the SNP line at small amplitudes of the RF field is determined by the amplitude of the RF field, while the intensity of the SNP spectral line depends on this amplitude according to a law describing diffusion motion. The use of a delay between the laser and RF pulses should not result in a substantial narrowing of SNP lines. This is due to the fact that the re-encounter of partners in radical pairs which takes place after a prolonged diffusion walk contributes significantly to the SNP. As long as the delay τ differs from zero, this contribution remains crucial. The variation of the intensity of the SNP line in the magnetic field corresponding to the resonance line maximum vs. the delay τ appears the most informative. For great delays, the dependence typical of diffusion motion should be observed. The SNP kinetics calculated using the two-position model is described by an exponential curve with a characteristic exponent parameter equal to the constant for the irreversible decay of radical pair τ_c . The expected line widths in the SNP spectrum should not depend on the amplitude of the RF field and are determined by the reciprocal time $1/\tau_c$.

Time-resolved SNP experiments for geminate radical pairs in homogeneous solutions are currently impossible because the characteristic lifetime of radical pairs is about several nanoseconds and, to obtain real kinetics, it would be necessary to initiate the reaction by lasers with nanosecond pulse duration. In addition, it would be necessary to create a rise time of about 1 ns for the RF pulse, which is a difficult engineering problem. However, the lifetimes of short-lived biradicals and micellised radical pairs lie in the range from tens to hundreds of nanoseconds; the kinetics of these systems can be studied experimentally.

2. Stimulated nuclear polarisation of short-lived biradicals

Biradicals are formed as intermediates in many photochemical processes; therefore, it is important to investigate them in order to elucidate reaction mechanisms. As a rule, the lifetimes of flexible biradicals are about 0.1–1 μs . They are determined by the rates of intersystem crossing from the non-reactive triplet state to the singlet state, recombination from the singlet state and the conformational motion of radical centres. Photolysis of aliphatic cyclic ketones with rupture of the α -bond is a perfect method for the investigation of short-lived biradicals. The α -bond rupture occurs from the excited triplet state almost in all cases. The introduction of methyl or phenyl groups in the α -position decreases the activation energy and increases the rate of α -rupture to 10^9 s⁻¹ or more. The acylalkyl biradical thus formed can be decarbonylated giving rise to alkyl biradicals. The rate of decarbonylation increases substantially upon α -substitution. For biradicals formed in the photolysis of aliphatic cyclic ketones, the rate of molecular motion in non-viscous solutions at room temperature is much higher than the rate of spin dynamics. In the absence of steric hindrance, recombination from the singlet state is not the rate-determining step either; thus, the lifetime of biradicals is determined by the rate of the triplet–singlet conversion, which depends on the hyperfine electron-exchange and spin-orbital interactions and on the electron spin relaxation.

The main features of the generation of SNP in biradicals have been studied experimentally in relation to the photolysis of several aliphatic cyclic ketones $\text{O}=\text{C}(\text{CH}_2)_n$ ($n = 10\text{--}13$).^{86, 96–99} As noted above, the major pathway of the photolysis of cycloalkanonones is α -rupture in the triplet-excited ketone, resulting in the formation of an acylalkyl biradical. Variation of the length of the polymethylene chain of the ketone, the HFC constants (by using ketones in which the protons in the α -position have been replaced by D or CH_3) and the external magnetic field, as well as detection of SNP from ^1H and ^{13}C NMR spectra make it possible to vary the ratio of A , J and B_0 over a broad range.

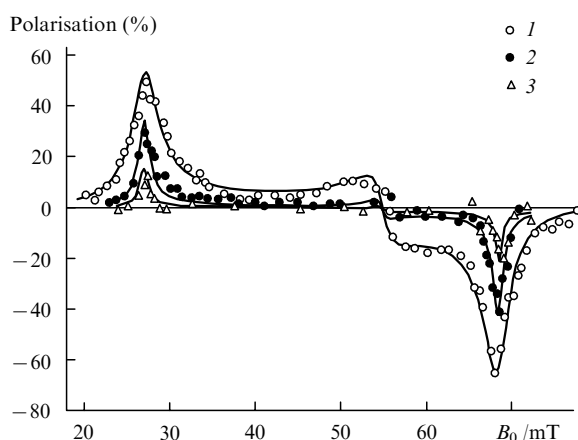


Figure 14. ^{31}P SNP spectra of radical pairs formed in the photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide. The spectra were detected using the NMR signal of diphenylphosphine oxide. Polarisation was measured in percent of the CIDNP for $B_0 = 43$ mT. B_1 (mT): (1) 1, (2) 0.6, (3) 0.4. The continuous lines are the spectra simulated using the analytical formula for weak magnetic fields.⁷³

For biradicals with $n = 10-13$ in weak magnetic fields (3–12 mT), the S–T₋ channel of intersystem crossing predominates. Both emission CIDNP and emission SNP can be observed in the NMR signals of all groups of protons of ketones and aldehydes. Polarisation on the ketone γ -protons, for which the HFC constant in the biradical is close to zero, arises due to the transfer of the nuclear polarisation from the α -CH₂ groups of the ketone, induced by the transfer of the sample from a weak to a strong magnetic field. For ketones with $n = 11-13$ in a ~ 50 mT field, the main intersystem crossing channel is S–T₀; no signals for the ketone protons are observed in the SNP spectra in this field because the HFC constants of α - and β -protons in biradicals have different signs, and the lines for opposite signs overlap. When the chain length decreases, the effective value of exchange interaction increases; an emission SNP spectrum is obtained in a 50 mT field for biradicals formed in the photolysis of cyclodecanone ($n = 10$). Koptug *et al.*⁹⁶ reported calculations of SNP of short-lived biradicals performed for a realistic model, which had been used previously¹⁰⁰ to describe the field dependences of CIDNP. Presumably, exchange interaction occurs through the spatial overlap of the orbitals of unpaired electrons and is attenuated according to an exponential law as the distance r between the electrons increases

$$J(r) = J_0 \exp(-\alpha r),$$

the interaction anisotropy being averaged due to the fast rotations of the terminal groups of the polymethylene chain. Two mechanisms of electron spin relaxation were taken into account, one due to fluctuation of local magnetic fields and one, due to dipole–dipole interaction of the spins of the unpaired electrons. The pattern of the calculated SNP spectra is highly sensitive to the exchange interaction constant J_0 . Using experimental and theoretical spectra obtained for different radio frequencies, the optimal values for J_0 and α were found. Koptug *et al.*⁹⁶ studied theoretically the influence of several parameters, namely, the diffusion coefficient, the rate of trapping of biradicals, the rate of decay of the triplet biradical due to the spin-orbital interaction, and the electron spin relaxation, on the pattern of the SNP spectra. It is significant that all parameters, except the diffusion coefficient, have little influence on the shape of spectral lines but can only cause a decrease in the signal intensity. As noted above, the dependence of the signal intensity in the SNP spectrum on the delay τ bears information on the lifetimes of radical pairs. For instance, this dependence has been used⁹⁶ to estimate the lifetimes of short-lived biradicals formed upon photolysis of cyclodecanone. The characteristic times of SNP decay were ~ 80 ns. Due to the lack of a theory of time-resolved SNP for biradicals, the researchers could not use the experimental data to perform a profound analysis or to gain new information.

The kinetics of SNP of short-lived acylalkyl biradicals in homogeneous solutions in weak magnetic fields (~ 10 mT) have been studied.^{27, 101} Two types of radio-frequency pulses were used, a long pulse (~ 2 μ s) and a short pulse with a duration at half-height of 15 ns. It was shown that the kinetic dependences of SNP pass through a maximum when the delay between the laser pulse and the RF pulse is 40 ns and then decay by an exponential law. The appearance of the maximum is due to the competition between spin-dependent and spin-independent channels of the triplet–singlet conversion. The kinetics of SNP were described using a simple kinetic model. From comparison of the experimental data with the calculated data, the researchers estimated the rate of spin-orbital interaction, the electron relaxation rate and the lifetimes of the excited triplet molecules of ketones. Upon the addition of a quencher for triplet states (*cis*-piperylene), the time for attenuation of the SNP signal diminishes to reach a limiting value equal to the lifetime of the biradical. Proceeding from these results, the lifetimes of biradicals (80 ns for cyclododecanone and 50 ns for cycloundecanone) and of triplet molecules (250 ns for cycloundecanone and 150 ns for cyclododecanone) were estimated.

The ¹³C SNP spectra of acylalkyl biradicals with $n = 11$, in which the ¹³C isotope occurs in the carbonyl position or in the α -position, differ significantly. This is due to the difference between the HFC constants and, correspondingly, different ratios of the external magnetic field to the HFC constants, resulting in dissimilar efficiencies of the competing intersystem crossing channels.¹⁰² As shown by calculations performed in terms of the two-position model in weak and zero magnetic fields, the pattern of the SNP spectra of short-lived biradicals is exceptionally sensitive to the rate of spin-non-selective intersystem crossing; this can be used to measure their rates.

The main regularities of the origination of SNP in the consecutively formed biradicals were studied experimentally and theoretically¹⁰³ in relation to the acylalkyl and bisalkyl biradicals formed in the photolysis of tetramethyl-substituted cycloalkanes with $n = 11-15$. A specific feature of the consecutive biradicals, as well as of the consecutive radical pairs, is the ‘memory effect’, which implies that nuclear polarisation of the diamagnetic products of the secondary radical pairs or biradicals reflects the spin dynamics processes in both the primary and the secondary pair (biradical). Due to the high spectral selectivity, typical of the NMR method, when recording the NMR spectra of various recombination products, the authors were able to obtain simultaneously the SNP spectra of primary and secondary biradicals arising during photolysis. A model for the calculation of SNP for the consecutive biradicals was developed; the generation of SNP was studied both experimentally and theoretically. The main characteristics influencing the line intensity and the pattern of the SNP spectra of secondary biradicals are the rate constant for the electron relaxation of both biradicals, the time required for relaxation processes, the rate constant for the spin-orbital interaction, parameters of the exchange interaction of both primary and secondary biradicals, the rate constant for decarbonylation, the type of the main intersystem crossing channel in the biradicals, and the ratio of the polarisation intensities for the first and the second biradicals. Note that for the symmetrical biradicals, in which the HFC constants for various radical centres are equal, the SNP spectral pattern differs appreciably from the case considered above. This is due to the fact that, in symmetrical biradicals or radical pairs in strong magnetic fields, the SNP effect is equal to zero. This fact can be easily understood from a qualitative consideration. Saturation of the electron transitions in radical pairs with identical orientations of nuclear spins does not accelerate the intersystem crossing. In the radical pairs with the opposite orientation of nuclear spins, the S–T conversion is accelerated for both sub-ensembles of radical pairs. Thus, the overall polarisation induced by a microwave field would be equal to zero. When calculating the SNP in symmetrical biradicals in weak magnetic fields, it is necessary to take into account both HFC constants in the secular approximation. If one HFC constant is taken into account in the secular approximation, while the second, is in a non-secular approximation, a non-symmetrical radical pair is actually considered and an S–T₀ type spectrum appears in the calculated SNP spectra. Unlike biradicals with different HFC constants, for which the spectral pattern is determined by the major channel of the singlet–triplet conversion, for symmetrical biradicals, the SNP spectra would always correspond to the S–T₋ type even in those cases where S–T₀ is the major channel of intersystem crossing.

Study of the SNP of acylalkyl and bisalkyl biradicals in different magnetic fields (Fig. 15) allowed the authors to determine the J_0 value, which describes adequately all the experimental data. In the photolysis of ketones with $n = 11$, on the basis of the NMR signals of the products resulting from the bisalkyl biradicals, the S–T₋ type spectra represented by one emission line ($B_0 = 54.6$ mT) were observed (Fig. 15c). For $n = 12$, inverted S–T₀ type spectra were recorded (Fig. 15d). The lower limit of the J_0 range was established by comparing the calculated and experimental SNP spectra of biradicals with $n = 11$ (S–T₋ type), while

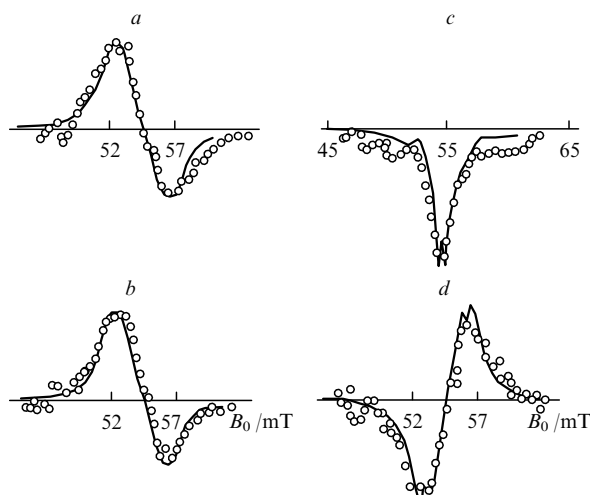


Figure 15. Experimental (dots) and calculated (continuous lines) SNP of acylalkyl $[\text{OC}^*\text{CMe}_2(\text{CH}_2)_{n-2}\text{C}^*\text{Me}_2]$, $n = 11$ (a), 12 (b) and bisalkyl $[\text{MeC}^*(\text{CH}_2)_{n-2}\text{C}^*\text{Me}_2]$, $n = 11$ (c), 12 (d) biradicals formed in the photolysis of tetramethyl-substituted cycloalkanones.

the upper limit was found by comparing the spectra of biradicals with $n = 12$ (S– T_0 type) in a 27 mT field.

In the literature, the short lifetime of the acylalkyl biradicals is attributed most often to the presence of spin-orbital interaction between the radical centres of the biradical (see, for example, Ref. 104). This statement is true for biradicals with relatively short chains ($n = 5, 6$). Evidently, the influence of spin-orbital interaction on the lifetime of the biradical depends on the residence time of radical centres in the reaction volume. For biradicals with long chains, the residence time of the radical centres in the reaction area is short; therefore, the role of relaxation occurring due to spin-orbital interaction should markedly decrease. On the basis of analysis of the SNP experimental kinetics for biradicals with $n = 12$ –15, 17, it was concluded that in addition to the spin-orbital interaction, spin-rotational relaxation also plays an important role.¹⁰³

The influence of temperature and viscosity on the spin and molecular dynamics of short-lived alkylacyl and bisalkyl biradicals formed successively has been studied both experimentally and theoretically.¹⁰⁵ The ^1H and ^{13}C CIDNP and SNP effects were studied in the temperature range from 200 to 360 K for magnetic fields varying from 0 to 0.1 T. The investigators found a unified set of parameters that describe adequately the nuclear polarisation effects for both protons and ^{13}C atoms with different HFC constants in the biradical. The introduction of a temperature dependence of the biradical reactivity proved especially important for attaining quantitative agreement between the calculated and experimental data in the low-temperature range. Comparison of the experimental data with the results of model calculations showed that broadening of the field dependence of CIDNP and slowing down of the decay of SNP signals at temperatures below 240 K is due both to the retardation of the molecular mobility of the polymethylene chain and to the decrease in the reactivity of the acylalkyl biradicals. For the bisalkyl biradicals, spin-orbital interaction is less important for the spin dynamics than in the acylalkyl radicals. The effect of molecular dynamics on the field dependences of the CIDNP of the products formed from bisalkyl biradicals with the change in temperature is more pronounced. Since the lifetime of bisalkyl biradicals is much longer than the lifetime of acylalkyl biradicals, the intensity of nuclear polarisation of the products formed from bisalkyl biradicals is much higher.

3. Stimulated nuclear polarisation of micellised radical pairs

Micellar solutions as a specific microstructured medium have been drawing attention of photochemists during the last decades. Numerous publications^{106–115} are devoted to the detection and investigation of extremal magnetic effects and magnetic isotope effects, nuclear and electron polarisation and other effects in radical pairs located in micelles. In micelles, radical pairs are isolated; this enables detailed investigation of the geminate recombination of radicals and spin and molecular dynamics of radical pairs. Since in radical pairs occurring in micelles, the partners are located at short distances from each other throughout their whole lifetime, the electron exchange interaction has a considerable influence on the intersystem crossing in these radical pairs. The field dependences of ^{13}C CIDNP of radical pairs formed upon photolysis of dibenzyl ketone in sulfate micelles of different sizes have been studied.¹⁰⁸ The polarisation of the ^{13}C nuclei in both strong and weak fields (irrespective of the sign of the HFC constant) was found to be emission polarisation. The ‘maximum’ of the field dependence of CIDNP shifts upfield as the size of micelles decreases. On the basis of experimental data, it was concluded that CIDNP is mainly due to S– T_0 transitions. The effective exchange interaction estimated from the field dependence of CIDNP was ~ 30 mT. However, the results obtained by CIDEP for a number of systems are at variance with the conclusion concerning large values for average exchange interactions. In the EPR spectra of micellised radical pairs, each hyperfine-structure line is split into two. This splitting can be described by including a constant exchange interaction $|J| \approx 5$ –10 MHz into the Hamiltonian in model calculations.¹¹⁵ Similar estimates were obtained in RYDMR experiments in micelles.¹¹⁴ Later, it was shown that modulation of the exchange interaction due to the mutual motion of radicals should be taken into account in the description of the spectral patterns and the CIDEP kinetics of spin-correlated pairs in micelles.¹¹⁶ The use of the SNP method for the investigation of the effect of exchange interaction on the intersystem crossing in radical pairs confined in micelles proved quite effective.^{75–78, 117–123} Stimulated polarisation is detected from the NMR signals of the diamagnetic products of recombination of radical pairs; therefore, it reflects the influence of the exchange interaction on the intersystem crossing in radical pairs localised in micelles to a greater extent than CIDEP, in which the predominant contribution to the spectral signal is made by free radicals.

The ^{13}C and ^{31}P SNP techniques were used to study the radical pairs resulting from photolysis of α -methyldeoxybenzoin,^{77, 119, 122, 123} dibenzyl ketone,^{76, 78, 117, 118, 122} benzoin,⁷⁸ deoxybenzoin,¹²⁴ benzophenone in the presence of *tert*-butylphenol¹²¹ and (2,4,6-trimethylbenzoyl)diphenylphosphine oxide¹²⁰ in the sulfate micelles $\text{Na}^+\text{SO}_3^-\text{O}(\text{CH}_2)_n\text{Me}$ of various sizes ($n = 6$ –11). The significant differences in the ratios of the HFC constants and the lifetimes of these radical pairs permitted the researchers to examine the influence of the exchange interaction on the pattern of the SNP spectra. It was discovered that line splitting and line width in the spectra depend on the size of micelles. From comparison of the spectra recorded in strong and weak magnetic fields and the field dependences of CIDNP with the spectra calculated theoretically, parameters of the molecular and spin dynamics of micellised radical pairs were found.

The dynamics of radical pairs in micelles were described using a microreactor model — one radical was fixed in the centre of a spherical micelle, whereas the other was moving inside the micelle core.^{75–78} In addition, a diffusional character of the motion was assumed. The electron spin relaxation due to the dipole–dipole interaction and due to modulation of the anisotropic part of HFC was taken into account.⁷⁷ The allowance for the dipole–dipole relaxation was made by two methods. One approach is similar to that described previously⁶⁹ for the calculation of the field dependences of CIDNP and SNP in short-lived biradicals. The other approach is more consistent; it was used (in combination with the Monte Carlo method)¹²⁵ to calculate the correlation function of

the dipole–dipole interactions in radical pairs for micelles of different sizes. Subsequently, an analytical expression describing the dipole–dipole relaxation was obtained.¹²⁶ The main parameters determining the molecular dynamics of radicals are the coefficient of mutual diffusion D , the micelle radius L , the reaction radius and the rate constant for the radical exit to the bulk k_{ex} . Splitting in the SNP spectra depends on the ratio of the following values: the HFC constants, the characteristic time between the collisions of radicals inside the micelle

$$\tau_2 = \frac{L^3 - R^3}{3RD} \sim \frac{L^3}{3RD},$$

the exchange interaction and the rate of the spin-selective decay. Upon a decrease in the micelle size, the time the radical pair spends in the reactive state increases relative to the time spent in the non-reactive state. Thus, the time-average exchange interaction and the time-average recombination rate increase.

The experimental implementation of the SNP method for the investigation of radical pairs in micelles has several specific features. On the one hand, due to the higher viscosity of micellar media compared to homogeneous solutions, the nuclear relaxation time of diamagnetic products decreases, resulting in a less intense signal in the SNP spectra. On the other hand, the lifetime of radical pairs in micelles (~ 0.1 – 1 μs) is commensurable with the characteristic time of RF transitions (~ 10 – 100 ns), which is calculated from the expression

$$\omega_1 = \gamma_e B_1$$

(the B_1 value lies in the range 0.1 – 1 mT). This results in a pronounced increase in the intensity of spectral lines and provides the possibility of measuring ^{13}C SNP spectra for samples with natural abundance of ^{13}C . An advantage of the ^{13}C SNP method is that the spectra of radical pairs containing ^{13}C magnetic nuclei are recorded on the basis of the corresponding lines in the ^{13}C NMR spectrum; therefore, the splitting in the SNP spectrum is equal to the HFC constant for this nucleus in the radical.

In small micelles ($n = 7$ – 9) for $A = 2$ – 10 mT, the decrease in the spectral splitting is due to both the exchange interaction J and the rate of spin-selective decay of the radical pair. In larger micelles ($n = 11, 12$) for $A > 2.0$ mT, splitting in the spectrum is equal to the HFC constant, exchange interaction influencing only the widths of individual lines.

The ^{13}C SNP effects involved in the photolysis of α -methyldeoxybenzoin enriched to 96% in the ^{13}C isotope at the carbonyl position have been studied in micelles of different sizes.^{51,77} The splitting in the SNP spectrum for sodium dodecyl sulfate micelles amounts to 12.4 mT; it is equal to the HFC constant for the carbonyl carbon atom in the benzoyl radical (Fig. 16*a*). A decrease in the length of the polymethylene chain of the detergent molecule results in a shorter spacing between the lines in the SNP spectrum and in a changed width of individual lines. From calculations of the SNP spectra and field dependences of CIDNP, the optimal parameters of the electron exchange interaction and spin-selective decay were found ($k_s\tau$): $J_0 = 50$ mT (the parameter for the decay of exchange interaction α is 2 Å) and $k_s\tau = 8$. It is noteworthy that the high sensitivity of the SNP spectra to the change in the rate of re-encounters of radicals in the micelles and, hence, to the change in the intra-micellar viscosity and micelle size can be used to investigate the dependence of the properties of micelles on the temperature and on salt additives (see Fig. 16).¹²³

Parnachev *et al.*¹²¹ studied experimentally the SNP of radical pairs formed in the photolysis of benzophenone- d_{10} in sodium dodecyl sulfate micelles in the presence of 2,4,6-tri-*tert*-butylphenol with the natural abundance of the ^{13}C isotope. On exposure to a 0.03 mT radio-frequency field, the NMR spectrum exhibits signals from six radical pairs differing in the position of ^{13}C (denoted by the Roman numerals I–VI) (Fig. 17*a*).

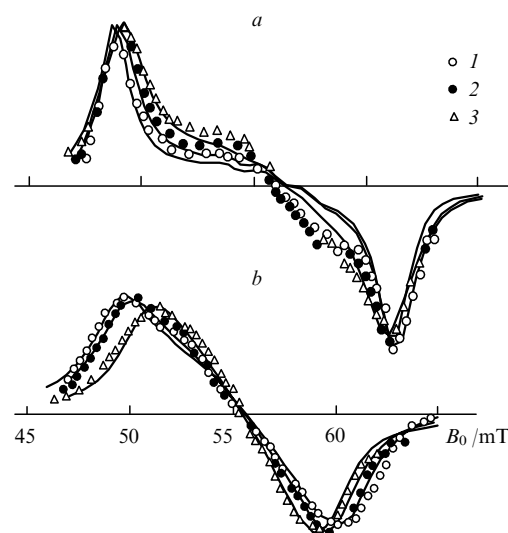
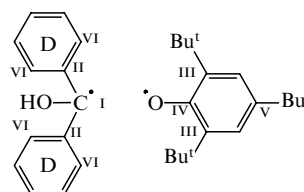


Figure 16. Temperature dependence of the SNP spectra of the radical pairs formed in the photolysis of α -methyldeoxybenzoin in sodium dodecyl sulfate (*a*) and sodium octyl sulfate (*b*) micelles. The spectra were detected using the NMR signal of the carbonyl carbon atom of α -methyldeoxybenzoin. The continuous lines are the calculated SNP spectra. T ($^{\circ}\text{C}$): (1) 12, (2) 29, (3) 45 (*a*) and (1) 10, (2) 17, (3) 45 (*b*).



The SNP spectra were obtained for all the six radical pairs with different positions of ^{13}C . Figure 17*b* shows the SNP spectra for pairs with the ^{13}C isotope in positions I and II. The opposite phases of these spectra are due to the different signs of the HFC constants for the corresponding ^{13}C nuclei. Measurement of the SNP kinetics makes it possible to determine the lifetimes of radical pairs and to draw conclusions about the mechanisms of their relaxation. The value of the contact electron exchange interaction estimated from comparison of the experimental and theoretically calculated spectra is $|J_0| > 40$ mT. The HFC constants in radical pairs with different positions of the ^{13}C isotope were calculated from analysis of the SNP spectra.

In the limiting case, where the characteristic time of intersystem crossing markedly exceeds the characteristic time period between the re-encounters in the micelle ($A\tau_2 \gg 1$), splitting of lines in the SNP spectra does not depend on the micelle size, and the effect of the exchange interaction reduces to line broadening.¹²⁰ For example, this is the case in the radical pairs formed in the photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide. In accordance with theoretical predictions, the experimental SNP spectra of radical pairs in sodium octyl sulfate micelles and in sodium dodecyl sulfate micelles show the same splitting; however, agreement between experimental and theoretical spectra is attained only when sodium dodecyl sulfate micelles with a radius of 17–21 Å or sodium octyl sulfate micelles with a radius of 13–15 Å are used. Thus, it was concluded that the effective radius of micelles varies depending on the compounds involved in the reaction.

As noted above, in measuring the EPR spectra, the observed polarisation contains contributions of both radical pairs in micelles and free radicals, whereas SNP arises only in the presence of radical pairs. For example, using SNP and time-resolved EPR, the spectra of the radical pairs formed in the photolysis of α -methyldeoxybenzoin and benzoin in micelles of various size

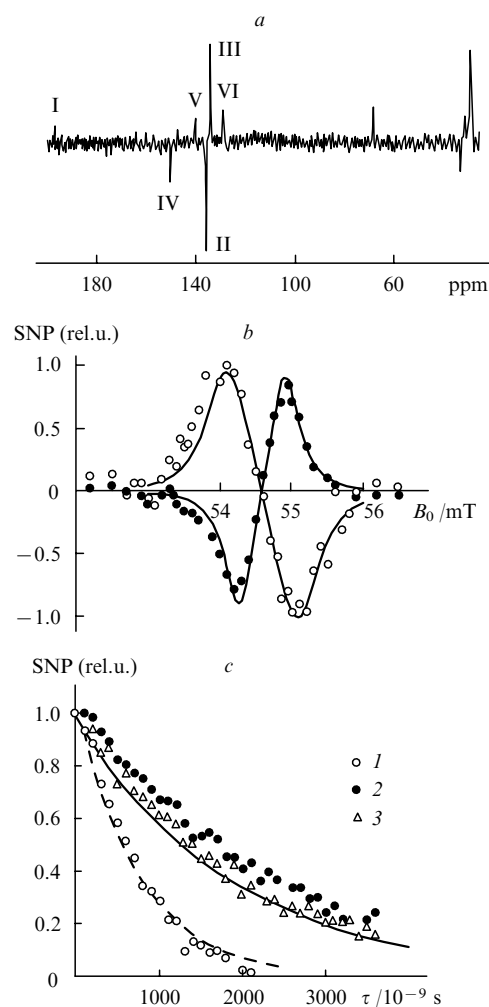


Figure 17. NMR spectrum of radical pairs formed in the photolysis of benzophenone- d_{10} with 2,4,6-tri-*tert*-butylphenol in the micelles on exposure to a 0.03 mT RF field (a); SNP spectra of radical pairs labelled at position I (1) and II (2) (b) and the kinetic curves of SNP of the radical pairs labelled at positions I–III (1–3, respectively) (c) in different magnetic fields. B_0 (mT): (1) 53.5; (2), (3) 54.1. The calculated relaxation constants k_{rel} 1.2×10^6 (dashed line) and 3.0×10^5 s $^{-1}$ (continuous line).

were recorded. The SNP spectra measured for micelles with different sizes are closely similar because the HFC constants, electron relaxation parameters, radical size, and the reactivity of radical pairs are very close. Meanwhile, the EPR spectra recorded for the photolysis of α -methyldeoxybenzoin and benzoin are different in principle. Whereas the RP formed in α -methyldeoxybenzoin is responsible for an antiphase structure of the spectrum depending on the micelle size, in the case of benzoin, no line splitting due to exchange interaction is observed.¹¹⁶ The radical pairs consisting of hydroxybenzyl radicals formed in benzoin photolysis leave the micelles at a markedly higher rate than the radical pairs consisting of benzyl and benzoyl radicals. As shown by Tarasov *et al.*,¹¹⁶ within 200 ns after the photolysis of α -methyldeoxybenzoin, 70% of the radicals are located in micelles, while in the case of benzoin, this value is only 5%.

The kinetics of micellised radical pairs have been studied by time-resolved SNP. It is obvious that the coherent transitions between singlet and triplet sublevels in radical pairs cannot be described within the framework of a kinetic scheme.¹²⁴ However, since for most radical pairs, the rate of recombination markedly exceeds the relaxation rate, the experimental kinetic dependences of SNP are well described by an exponential curve and are consistent with the calculation based on the simple kinetic scheme.

Yet another approach to the theoretical description of the dynamics of radical pairs is numerical solution of the Liouville equation for the density matrix.⁷⁸ The kinetic curves for time-resolved SNP measured for the photolysis of α -methyldeoxybenzoin and dibenzyl ketone in sodium dodecyl sulfate micelles are described adequately by an exponential function in accordance with the kinetic scheme.

Figure 17c shows the kinetic curves of SNP obtained for the photolysis of benzophenone- d_{10} with 2,4,6-tri-*tert*-butylphenol in sodium dodecyl sulfate micelles. The SNP kinetic curves for radical pairs labelled in positions I–V bear information on the relaxation in various radical pairs. The decay of SNP for the pairs labelled in positions II–V is due to the exit of radicals from the micelle and dipole–dipole relaxation. For a pair labelled in position I, relaxation caused by the modulation of the anisotropic part of HFC plays an important role.

In the photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide, the rate of the decay of SNP kinetics for sodium dodecyl sulfate micelles is 2.5 times higher than that for sodium octyl sulfate; meanwhile, in the case of photolysis of ketones, this difference was not more than 20%–30%. Analysis of the resulting time dependences in terms of the kinetic model made it possible to estimate the relaxation and recombination rates for the radical pair in this reaction. For sodium octyl sulfate micelles, the relaxation rate is only 1.8 times lower than that for sodium dodecyl sulfate micelles. Thus, the SNP kinetics observed in sodium octyl sulfate micelles is determined by both recombination and relaxation. Note that the parameters determining the kinetics of radical pairs and those determined from theoretical and experimental SNP spectra are in good agreement with the data from the time-resolved EPR spectra.^{127, 128}

The use of the SNP methods in investigating micellised radical pairs provides unique information on their spin dynamics and kinetics. This possibility is due to the high sensitivity of the SNP method and to its selectivity with respect to radical pairs. The information obtained in SNP studies of micellised radical pairs was used in experiments on the measurement of the magnetic isotope effect (MIE) induced by a resonance RF field. The reaction investigated in these experiments was photolysis of dibenzyl ketone.¹²⁹ Saturation of the electron transitions in radical pairs can give rise to enhanced MIE in two different regimes: at small amplitudes of the RF field ($B_1 \ll A$), the S–T conversion in one sub-ensemble of radical pairs containing a magnetic isotope is accelerated, while at large amplitudes of the RF field ($B_1 \gg A$), closing of the S–T conversion for radicals devoid of a magnetic isotope takes place. Tarasov *et al.*¹²⁹ used the former regime but the latter appears to be more promising as regards enhancement of MIE.^{130, 131} The SNP method can provide exact information on the RF-field amplitude that ensures the maximum MIE value.

V. Chemically induced dynamic nuclear polarisation in switched external magnetic fields

The method of time-resolved CIDNP permits one to obtain quantitative information about the kinetics of radical reactions, lifetimes of triplet molecules and electron–nuclear cross-relaxation processes.^{132–135} The procedure involved in the time-resolved CIDNP method is the measurement of the dependence of CIDNP intensity on the variable delay τ between the laser pulse and the detecting radio-frequency pulse (90-degree pulse of an NMR spectrometer) (Fig. 18a). CIDNP arises in the strong magnetic field of the NMR spectrometer; as a rule, this is not the optimal field for observing this effect when many photochemical reactions take place. The time resolution of the method is determined by the duration of the radio-frequency pulse and is equal to 40 ns at best (normally, it is of the order of microseconds). It is often necessary to study CIDNP in weak and medium magnetic fields⁵² because this method can provide information about the exchange interaction, exchange reactions and so on. When measuring CIDNP in

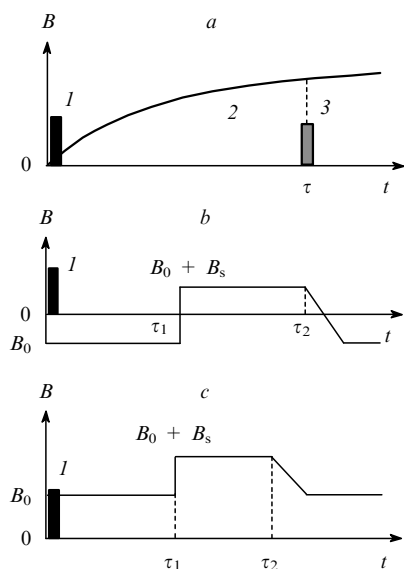


Figure 18. Schematic illustration of time-resolved CIDNP (a) and switched external magnetic field CIDNP (b, c); (1) laser, (2) region of CIDNP generation, (3) detecting radio-frequency pulse. Field switching can occur both with (b) and without (c) change in its direction.

weak and medium magnetic fields, photolysis is normally carried out in the field of a separate magnet and then the sample is transferred into the probe of an NMR spectrometer to record the spectrum. Photolysis can be performed directly in the probe of an NMR spectrometer with detection in weak magnetic fields;¹³⁶ however, in this case, spectral resolution and the sensitivity are very low, which restricts the scope of this method to systems with abnormally high CIDNP intensity. It is evident that time resolution by a traditional time scheme cannot be used in the experiments with transfer of the sample from the field of an individual magnet to the probe of an NMR spectrometer. This opportunity appears in the case of fast switching of the magnetic field within a variable period after the laser pulse initiating the radical reaction (Fig. 18 b, c). The idea of switching the external magnetic field (SEMF) during a photochemical reaction was first proposed and implemented by Lavrik *et al.*¹³⁷ The authors studied the effect of magnetic field switching on the intensity of fluorescence of excimers in radical-ion reactions. On the basis of the results obtained, estimates were made of the lifetimes of radical pairs.

The potential of the methods based on the SEMF during the lifetime of radical pairs was studied theoretically.⁸³ The researchers considered the influence of SEMF on both the probability of recombination of radical pairs and the nuclear polarisation of diamagnetic products in strong magnetic fields (*i.e.* with allowance for only $S-T_0$ transitions). Three different modes of radical recombination were chosen. In the first mode, the singlet-triplet transitions occur in the period between two contacts. This is accompanied by quantum oscillations. In the second mode, the $S-T_0$ transitions do not have time to take place in the interval between two contacts but do occur effectively over the lifetime of the pair in the cage. In this case, no quantum oscillations are displayed; however, the recombination kinetics depend on the frequency of $S-T_0$ transitions. Finally, in the third mode, the singlet-triplet transitions are relatively ineffective. This mode of recombination is of interest because it permits one to determine the lifetime of the pair in the cage. It should be noted that in experiments, the recombination mode is largely 'controllable'. It can be changed, for example, by changing the solution viscosity.

Bagryanskaya *et al.*¹³⁸⁻¹⁴⁰ carried out experiments based on switching of the external magnetic field within a variable period after a laser pulse followed by recording of the CIDNP effect (the SEMF CIDNP method). It was found that the change of nuclear

polarisation of the products of radical reactions upon switching the external magnetic field can be induced both by the change in the conditions of spin dynamics of radical pairs and intermediate short-lived free radicals and by the change in the electron and nuclear polarisation at the instant of switching. On the one hand, this treatment substantially complicates interpretation of the experimental results but, on the other hand, it opens the following ways for the investigation of the chemical kinetics and spin dynamics of radical species.

(i) Study of the dependence of polarisation on the delay τ between the laser pulse and the instant of magnetic field switching allows one to explore the kinetics of CIDNP of geminate radical pairs. The time it takes to switch a magnetic field by 10^{-3} T equals 1–3 ns. The time resolution is determined by the accuracy of synchronisation of the laser pulse and the instant of magnetic field switching (20–30 ns). Unlike the traditional time-resolved CIDNP, this method allows investigation of the CIDNP kinetics in weak and medium magnetic fields. This time resolution in NMR spectrometers is, in principle, impossible in weak fields because it is determined by the duration of the radio-frequency pulse, which lies in the millisecond time interval for weak and medium fields.

(ii) Variation of the delay τ permits one to change selectively the conditions of spin dynamics for geminate and diffusion radical pairs and thus to study the chemical kinetics of radical species.

(iii) Switching of the magnetic field changes the electron and nuclear polarisation of free radicals; this makes it possible to study the mechanisms of electron relaxation and the electron-nuclear cross-relaxation and CIDEP in weak magnetic fields.

Since the change in the magnetic field by $\sim 10^{-2}$ T causes only a minor change in the CIDNP in strong magnetic fields, realisation of the SEMF CIDNP technique in strong magnetic fields requires that a pulsed magnetic field of a substantial magnitude be created. This is a complex engineering problem. In weak magnetic fields, CIDNP changes quite substantially as the magnetic field changes by $\sim 10^{-3}$ T. The SEMF CIDNP method in weak and medium magnetic fields was implemented using a setup in which photolysis was carried out in the field of a separate magnet and, subsequently, after polarisation appeared, the polarised diamagnetic product was rapidly (over a period shorter than the characteristic time of nuclear relaxation) delivered *via* a fast-flow system to the probe of an NMR spectrometer in which CIDNP was recorded. The magnetic field is switched by use of Helmholtz coils, which create an additional field in the magnet with a switching amplitude of ± 7 mT. This markedly restricts the range of fields in which the SEMF CIDNP kinetics can be measured and is due to a requirement of the method according to which the absolute magnitudes of CIDNP in the initial and the final fields should be substantially different. Therefore, the highest sensitivity of the method is attained in those fields, in which the curve for the field dependence of CIDNP has 'steep slopes'.

1. Chemically induced nuclear polarisation under conditions of non-adiabatic switching of the magnetic field

The time of electron relaxation of free radicals does not actually depend on the switching of the external magnetic field. However, the situation changes if the chemical processes, for example DEE, influence the electron relaxation. For radical-ion reactions with DEE, the relaxation times in weak fields can be markedly dependent on the external magnetic field. As has been shown above, CIDNP in radical-ion reactions is influenced substantially by DEE reactions. The dependence of CIDNP kinetics on the concentration of the donor or acceptor molecules can be used to measure the DEE rate and to study the electron polarisation in weak magnetic fields.

The utility of the SEMF CIDNP method for measurement of DEE rates has been demonstrated in relation to the photoisomerisation of fumaronitrile with naphthalene in polar solvents.¹³⁹ Figure 19 presents the kinetic curves for the SEMF CIDNP of fumaronitrile and maleonitrile recorded for magnetic fields

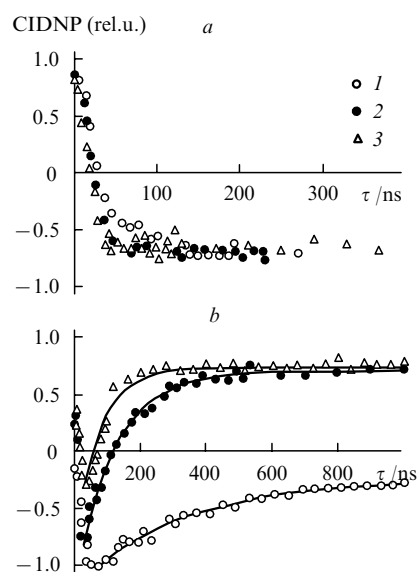


Figure 19. Kinetic curves of the SEMF CIDNP for the photoisomerisation of the fumaronitrile with naphthalene constructed using the NMR signals of maleonitrile ($B_0 = 1$ mT, $B' = -1$ mT) (a) and fumaronitrile ($B_0 = 3$ mT, $B' = 5$ mT) (b). Fumaronitrile concentration (mol litre $^{-1}$): (1) 5×10^{-3} , (2) 2×10^{-2} , (3) 4×10^{-2} .

switched either with or without inversion of their direction. The kinetics of CIDNP detected based on an in-cage reaction product, maleonitrile, are determined by the time required for the formation of radical pairs. For the escape reaction product, fumaronitrile, the kinetics are stipulated by the time of electron relaxation of the intermediate radical anion. The characteristic time of the decay of the CIDNP signal (of maleonitrile) is determined by the time of formation of geminate radical pairs; at high fumaronitrile concentrations $[(2-4) \times 10^{-2}$ mol litre $^{-1}]$ it amounts to 15–20 ns, while at low concentrations (5×10^{-3} mol litre $^{-1}$), it is 30–40 ns. On the basis of analysis of the kinetic curves of CIDNP constructed using the signals of maleonitrile in the NMR spectra, it was concluded that the time it takes for CIDNP in geminate radical pairs to appear is either shorter than or comparable with the duration of a laser pulse. Meanwhile, the kinetic curves of CIDNP detected from the NMR signal of fumaronitrile depend substantially on the rate of DEE. In the case of fast exchange, the obtained values coincide with the times of electron relaxation due to DEE, while for slow exchange, the CIDNP kinetics are determined by both the rate of DEE and the lifetime of free radicals.

It is worth noting that the typical lifetimes of radical pairs in homogeneous solutions are in the nanosecond range. Lasers with a pulse duration of 10–20 ns are used to initiate photochemical reactions; this stipulates the characteristic time of formation of the radical pair. Thus, experimental kinetic curves for CIDNP constructed for geminate radical pairs in homogeneous solutions are expected to reflect the kinetics of formation rather than the lifetime of the pair. The main advantage of the method discussed here is separation of the contributions of geminate and diffusion radical pairs to CIDNP.

The high time resolution and the possibility of investigating the kinetics of CIDNP in weak magnetic fields makes this method attractive for the investigation of spin dynamics of micellised radical pairs and short-lived biradicals. However, an attempt to carry out SEMF CIDNP experiments in micellised radical pairs demonstrated that, to obtain a satisfactory signal-to-noise ratio, the experiments should be carried out in fields whose magnitudes are close to the CIDNP maximum intensity. The field dependence of CIDNP for micellised radical pairs has almost in all cases the characteristic emission appearance, indicating the predominant

contribution of the $S-T_0$ transitions to CIDNP. Thus, the kinetics of SEMF CIDNP should also be calculated with allowance for $S-T_0$ transitions. This brought about the necessity of modifying the theory of CIDNP under conditions of SEMF for the case of radical pairs with limited mobility. This problem was successfully solved^{140, 141} on the basis of a kinematic approach. The time of switching of the magnetic field was assumed to be shorter than the time of intersystem crossing, electron relaxation and the exit of radicals from the micelles. To describe the motion of a micellised radical pair, the model for motion in the confined space was utilised. The calculation of the CIDNP effect as a function of the instant t_0 when the magnetic field is switched using typical parameters of a micellised radical pair showed that no quantum oscillations occur and the effect decays monotonically. The value by which the field changes has no influence on the pattern of time dependence, which is determined by the viscosity of the solution inside the micelle, but influences only the scale of the CIDNP effect. An interesting result is drawn if singlet–triplet transitions in one sub-ensemble of radical pairs stop after the magnetic field switching. In this case, quantum oscillations are observed on the time dependence of the effect. An expression was derived describing averaging of the $S-T_0$ transitions in the absence of relaxation and at low reactivity of the radical pair. In this case, conclusions about the character of movement of radicals in the radical pair can be drawn from the shape of the kinetic curve of SEMF CIDNP.

The purpose of the work by Fedin *et al.*¹⁴⁰ was to test the SEMF CIDNP method on a series of model reactions involving micellised radical pairs, to study the correspondence between the theoretical and experimental data, and to study the possibility of using this method for determination of the parameters of molecular and spin dynamics of micellised pairs. The researchers chose three photochemical reactions corresponding to different limiting cases of the ratio of the rates of radical exit from the micelles (k_{ex}), electron relaxation (k_{rel}) and $S-T_0$ conversion (k_{lc}) and conforming to the approximation at which only one magnetic nucleus is taken into account. In relation to these reactions, it was demonstrated that approximation of the kinetics by numerical calculations can provide information on the exit rate of the radicals from the micelle, the rate of decarbonylation, the rate of dipole–dipole electron relaxation, the rate of electron relaxation caused by anisotropy of HFC, and the rate of $S-T_0$ transitions occurring in the area of energy level crossing. Estimation of the rates of $S-T_0$ transitions for the systems studied suggested strong anisotropy of the exchange interaction.

The capacity of the SEMF CIDNP method for the investigation into short-lived biradicals has been evaluated¹⁴² taking photolysis of acylalkyl cyclic ketones as an example. The use of substituted ketones allowed the researchers to compare the CIDNP kinetics for biradicals differing only in HFC constants and to estimate the lifetime of the triplet molecule. The measurement of the lifetimes of short-lived biradicals formed upon photolysis of α,α -diphenylcyclododecanone showed that the kinetic curves of CIDNP for this reaction in weak magnetic fields are described with rather high accuracy by an exponential curve and the characteristic time of the curve decay coincides with the data obtained from the optical absorption of biradicals.

2. Chemically induced nuclear polarisation under conditions of adiabatic switching of the external magnetic field

Switching of magnetic field can be accompanied by the transfer of electron polarisation to the nuclei and *vice versa*. The time and conditions of magnetic field switching are important factors determining the type of polarisation transfer (adiabatic or non-adiabatic). It has been shown¹⁴³ that adiabatic switching of the magnetic field with the change in its direction results in the transfer of the integral electron polarisation to the nuclei. The effect of the adiabatic change of the external magnetic field on the transfer of integral CIDEP on the radical nuclei and the subsequent transfer to the diamagnetic products of radical chemical

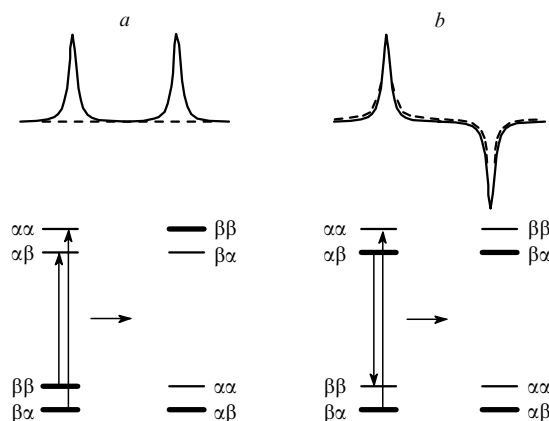


Figure 20. Schematic illustration of the effect of adiabatic switching of the external magnetic field on the nuclear polarisation of radicals; (a) the initial integral electron polarisation completely disappears after adiabatic switching of the magnetic field, (b) the initial multiplet electron polarisation does not change after the magnetic field switching.

reactions was studied. The limits of the adiabatic character of magnetic field switching were found from the Landau–Zener formula¹⁴⁴ to be 45–1100 nm. The lower limit is determined by the elucidation of time evolution of the spin system under adiabatic conditions, while the upper limit results from the requirement that radicals should react to give a diamagnetic product over a period of time shorter than the time of nuclear relaxation. The switching of the field was supposed to take place after the appearance of CIDEP. The adiabatic field switching is selective with respect to the mechanism of the appearance of CIDEP; the triplet and radical-pair mechanisms were considered as examples (Fig. 20). Passage through the zero magnetic field is accompanied by the transfer of the occupancy of levels: $\beta_e\alpha_n \rightleftharpoons \alpha_e\beta_n$ and $\alpha_e\beta_n \rightleftharpoons \beta_e\alpha_n$. It was found that the integral CIDEP is completely transferred to the radical nuclei and, after radical recombination, it can be detected in diamagnetic products. In the case of multiplet CIDEP, switching of the field does not influence the polarisation of the diamagnetic products. The optimal conditions for the transfer of electron polarisation were analysed numerically in the study cited as functions of the instant the field switching starts, of the duration of its front and of the velocity of passage through the zero-field region.

Evidently, non-zero nuclear polarisation is also transferred on electrons upon switching the magnetic field. This may result in the decay of escape nuclear polarisation. Since most radical reactions in weak magnetic fields are usually accompanied by substantial CIDNP, adiabatic change of the magnetic field can be used to separate the contributions of in-cage and escape polarisations. It has been shown¹³⁹ that transfer of electron polarisation to the nuclei takes place in weak magnetic fields even in the case of non-adiabatic switching of the magnetic field.

The potential of the SEMF ^1H CIDNP method as applied to short-lived radical species in a homogeneous solution has been analysed.¹⁴⁵ For this purpose, several photochemical reactions with participation of alkyl radicals PhCH_2 , Me_3C and PhC(O)CH_2 in magnetic fields of 0.5–2.5 mT were studied. From analysis of experimental data, it was concluded that the kinetics of polarisation is determined by the electron–nuclear relaxation in the intermediate radicals. The measured relaxation times of the PhCH_2 , Me_3C and PhC(O)CH_2 radicals in benzene were 2.2 ± 0.3 , 7.1 ± 0.3 and 1.2 ± 0.2 μs . Figure 21 shows the kinetic curves of CIDNP for the photolysis of dibenzyl ketone constructed using the NMR signals of dibenzyl ketone. The CIDNP kinetics for dibenzyl ketone is determined by the rate of decarbonylation of the phenacyl radical, whereas for dibenzyl, the decay of the kinetic curve does not depend on the initial concen-

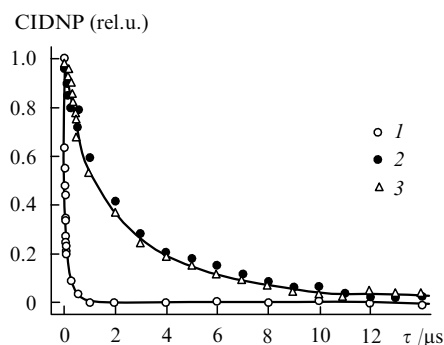


Figure 21. Experimental kinetic curves of SEMF CIDNP for the photolysis of dibenzyl ketone detected using the NMR signals of dibenzyl ketone (1) and dibenzyl: (2) I_1 , (3) $I_2 = 3I_1$.

tration of radicals and is equal to the electron relaxation time of the benzyl radical. The decays of the kinetic curves found for the photolyses of other compounds involving the benzyl radical do not depend on the initial concentration of the radicals either (Fig. 22).

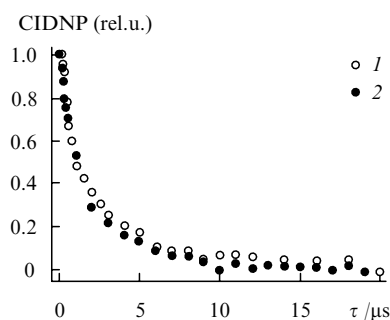


Figure 22. Kinetic curves of SEMF CIDNP for the photolysis of dibenzyl ketone (1) and deoxybenzoin (2).

The SEMF ^{31}P CIDNP method was used to determine the spin relaxation times for a series of phosphonyl radicals $\text{O}=\text{P(O)XY}$ (X, Y are various substituents) in a 5 mT field in acetonitrile and in dioxane. If the anisotropy of HFC is modulated only by the rotation of the radical as a whole with characteristic times of the order of several picoseconds, the relaxation time in acetonitrile should be shorter than that in dioxane. However, an opposite relationship was found in the experiment, which was explained by the occurrence of deformation vibrations with characteristic periods of several nanoseconds. It was found that, if the relaxation time of the radical is shorter than its lifetime, the kinetics of SEMF CIDNP are determined by relaxation.

3. Polarisation under conditions of double switching of the external magnetic field

Recently, further updating of the SEMF CIDNP method was proposed, which implies the use of two non-adiabatic magnetic field switchings separated in time during the reaction.¹⁴⁶ The researchers considered the variation of the polarisation of free short-lived radicals induced by double switching of the magnetic field and determined the dependence of CIDNP of the diamagnetic products on the delay between the switchings. The time diagram of the experiment is shown in Fig. 23a. In the first stage when $0 < t < t_1$, the radicals are formed under the action of a laser pulse in the external magnetic field H_1^0 . It is assumed that by the time instant t_1 , the primary polarisation of the radicals has arisen and they have moved out of the cage to the bulk. In the second stage when $t_1 < t < t_2$, the magnetic field undergoes a

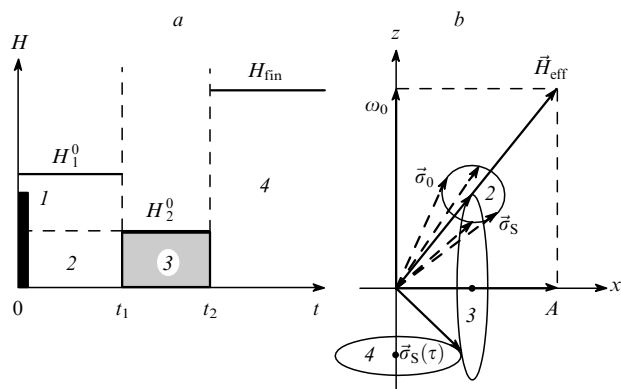


Figure 23. Time diagram (a) and vector model (b) in CIDNP experiments with double switching of the external magnetic field; (1) laser pulse, (2) preparation, (3) evolution; (4) recording.

non-adiabatic change to reach the value H_2^0 . The radical polarisation starts to oscillate, the characteristic frequencies of oscillation being dependent on the structure of the spin levels of the radicals in the field H_2^0 and on the level occupancies. Finally, in the third stage when $t_2 < t$, the field undergoes a non-adiabatic change to reach the value $H_{\text{fin}} \gg H_2^0$. The nuclear polarisation of the radicals ceases to change and, upon recombination, passes to the diamagnetic products. Thus, the polarisation of oscillations in the intermediate radicals can be recorded using the dependence of the CIDNP intensity of the recombination products on the delay $\tau = t_2 - t_1$.

The appearance of beats of the CIDNP of radicals and their diamagnetic products can be illustrated using a vector model (Fig. 23 b). For the case of radical with one magnetic nucleus with the spin $I = 1/2$, the two-level approximation $|\alpha\beta N\rangle, |\beta\alpha N\rangle$ and the vector model are applicable. According to Adrian's approach,¹⁴⁷ we consider the operators of the projections $\hat{F}_z, \hat{F}_x$ of the effective spin, which act on the basis functions $|\alpha\beta N\rangle, |\beta\alpha N\rangle$ as the corresponding Pauli matrices

$$\hat{F}_z|\alpha\beta N\rangle = \frac{1}{2}|\alpha\beta N\rangle;$$

$$\hat{F}_z|\beta\alpha N\rangle = -\frac{1}{2}|\beta\alpha N\rangle;$$

$$\hat{F}_x|\alpha\beta N\rangle = \frac{1}{2}|\beta\alpha N\rangle;$$

$$\hat{F}_x|\beta\alpha N\rangle = \frac{1}{2}|\alpha\beta N\rangle.$$

Then the Hamiltonian

$$\hat{H} = \omega_0 \hat{S}_z + A(\hat{S} \hat{I})$$

for the radical in question in a weak field determined in the subspace Ω with the basis set $|\alpha\beta N\rangle, |\beta\alpha N\rangle$ assumes the form

$$\hat{H} = A \hat{F}_x + \omega_0 \hat{F}_z = (\vec{H}_{\text{eff}}, \vec{F}),$$

where $\vec{H}_{\text{eff}} = (A, 0, \omega_0)$.

Thus, evolution of the state $|\Psi\rangle$ from the subspace Ω can be represented as precession of the effective spin $\vec{\sigma}$ in an effective magnetic field with the z component ω_0 , the x component A and

the frequency $\sqrt{\omega_0^2 + A^2}$ (see Fig. 23 b). The projection of the

vector $\vec{\sigma}$ on the z axis is equal to the difference between the occupancies of the levels $|\alpha\beta N\rangle, |\beta\alpha N\rangle$. The nuclear polarisation corresponding to the state $|\Psi\rangle$ is proportional to this value. The permanent generation of effective spins at the preparation stage results in the vectors $\vec{\sigma}_0$ covering uniformly the

surface of the cone, so that the average vector $\vec{\sigma}_S$ is directed along the cone axis, i.e. along the vector $\vec{H}_{\text{eff}}$. After non-adiabatic switching of the magnetic field to reach, for example, a zero magnitude, the vector $\vec{H}_{\text{eff}}$ is directed along the x axis and has the length A . At the initial instant, the vector $\vec{\sigma}_S$ remains constant then it starts to precess along the x axis with a frequency equal in magnitude to the HFC constant. The projection of the vector $\vec{\sigma}_S$ on the z axis varies periodically with the same frequency. If the magnetic field switches from the zero value to the value $H_{\text{fin}} \gg A$ after a time τ , the nuclear polarisation of radicals stops changing and passes to the diamagnetic reaction products after recombination. The vector $\vec{\sigma}_S$ would precess about the z axis and its projection on this axis would remain constant. Thus, by applying a second switching of the magnetic field after different delays τ , one can record the dependence of the oscillation of the CIDNP of diamagnetic products on τ . The paramagnetic relaxation in the radicals would result in a decrease in the length of the vector $\vec{\sigma}_S$ with an increase in the time t_1 and in a decrease in the amplitude of beats with an increase in the delay τ . When $t_1 \gg T_1$ (T_1 is the spin-lattice relaxation time), all the spin levels of the radical are almost equally occupied, which corresponds to the decrease in the length of the vector $\vec{\sigma}_S$ to zero. Evidently, in this case, the CIDNP of the diamagnetic products of the reaction does not oscillate. Thus, for high-quality recording of the oscillation, it is required that T_1 be much longer than t_1 .

Data on the oscillation of the CIDNP of the diamagnetic products bear information on the short-lived intermediates from which these products are formed. The amplitude, the frequency and the phase of oscillations depend on the structure and occupancy of the spin levels in the short-lived intermediate species. The method described above was first implemented by Makarov *et al.*¹⁴⁸ in relation to the photolysis of *p*-benzoquinone with 2-propanol- d_8 and to sensitised photoisomerisation of fumaronitrile. The oscillations of the CIDNP of the reaction products were

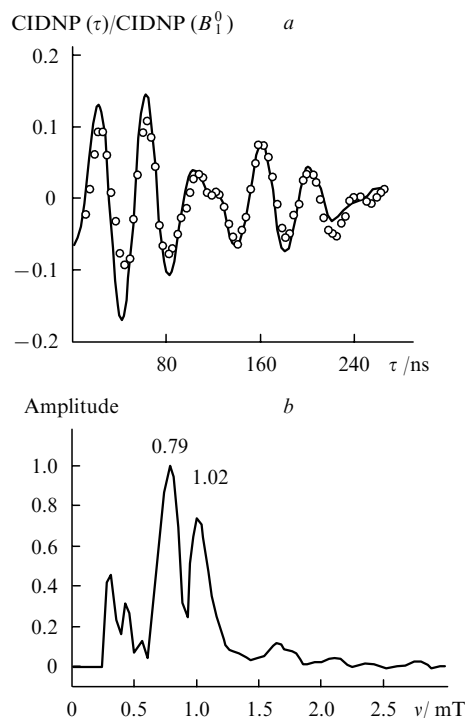


Figure 24. Oscillation of the CIDNP of the products of photolysis of *p*-benzoquinone with isopropanol- d_8 in acetonitrile in experiments with double switching of the external magnetic field (a) and Fourier spectrum of the resulting kinetic curve (b). The experimental positions of the resonance frequencies in the spectrum are given (the calculated positions are 0.76 and 1.04).

recorded as functions of the delay τ between the magnetic field switchings (Fig. 24). It was found that the amplitude, phase and the frequency of CIDNP beats are determined by the hyperfine structure and by the occupancies of the spin levels in the intermediate radicals. It was concluded from comparison of the experimental and theoretical data that the electron polarisation of semiquinoid radicals and fumaronitrile radical ions in weak magnetic fields is negative. It appears promising to use this method for investigating electron polarisation and the times of electron–nuclear relaxation of short-lived radicals in weak magnetic fields to which conventional time-resolved EPR is inapplicable.

VI. Conclusion

A vast body of experimental information has been accumulated on the use of high-sensitivity magnetic-resonance techniques based on the influence of variable resonance magnetic fields and switched constant magnetic fields on the nuclear polarisation of the products of radical reactions. The examples given in this review demonstrate the applicability of these methods to the study of the mechanism of radical reactions, identification of latent radical stages and measurement of DEE rates. The main regularities of polarisation of radical species with a broad range of lifetimes and in homogeneous and molecular-organised media have been elucidated. By now, the theory of the influence of RF fields on the nuclear polarisation in radical reactions has been thoroughly developed and employed to gain information on short-lived radical species — their spin dynamics and chemical kinetics.

The time-resolved SNP method can be used to separate the contributions to the polarisation of geminate and diffusion radical pairs and to obtain quantitative data on their kinetics. The SEMF CIDNP technique provides the possibility of measuring the rates of DEE, the kinetics of radicals, the lifetimes of short-lived biradicals and micellised radical pairs. This can prove useful in those cases where the use of flash photolysis is difficult due to the overlap of optical absorption bands. An additional advantage of the SEMF CIDNP method is the spectral resolution of NMR, which allows one to follow the transformation of biradicals into diamagnetic products. The DNP method provides the possibility of measuring the electron relaxation times for short-lived radicals and the signs and magnitudes of their HFC constants. Detection of DNP of the final reaction products can be used to investigate the mechanisms of radical processes. Unlike the CIDNP method, in the case of DNP, the formation of radical pairs in solution is not necessary. The doubly switched external magnetic field CIDNP method is supposed to be suitable for measuring the kinetics and the spin relaxation times of radicals, for investigating the CIDEP in weak magnetic fields, and for gaining information on the occupancy of the spin levels in the radicals.

Thus, nowadays, there exists a basis for the use of highly sensitive magnetic-resonance methods in the studies of complex photochemical reactions. The highest efficiency in the application of these methods can be attained by combining them with the techniques of laser flash photolysis and time-resolved EPR.

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Reagents for the preparation and cleavage of 1,3-dithiolanes

A K Banerjee, M S Laya

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Abstract. Data on procedures for protection of the carbonyl group by its conversion into the 1,3-dithiolane moiety and on cleavage of the latter under the action of different reagents are surveyed. The preparation of 1,3-dithiolanes from carbonyl compounds followed by deprotection can be used in syntheses of various organic compounds. The bibliography includes 54 references.

I. Introduction

Syntheses of organic compounds, including natural products, often generate a need to use protective groups. Thus if it is necessary that the reaction proceed selectively at one of several reaction centres of a polyfunctional compound, all other centres should be temporarily blocked. A good protective group must be removed selectively and quantitatively under the action of readily accessible reagents which do not react with functional groups to be regenerated. Various protective groups have already been developed and these investigations are being continued. Analysis of the published data demonstrated that the introduction and removal of a protective group is often a complex multistep process.

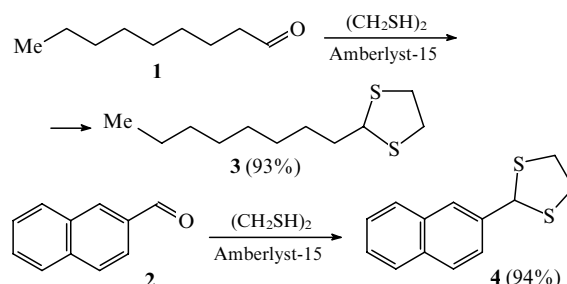
In the synthesis of particular carbonyl-containing products, it is sometimes necessary to prevent the reaction of the carbonyl group with reducing agents of acidic or alkaline nature, catalytic reducing agents and hydrides, some oxidising agents, strong and moderate nucleophiles, organometallic compounds, *etc.* In the reactions of polyfunctional organic compounds, it is very convenient to protect the carbonyl group by converting it into the 1,3-dithiolane moiety because sulfur-containing functional groups are inert with respect to many reagents. Various reagents, which are stable under conventional reaction conditions, have been developed for the synthesis of 1,3-dithiolanes.^{1,2} Generally, 1,3-dithiolanes are prepared by condensation of carbonyl compounds with 1,2-dithiols catalysed by protic or Lewis acids.^{3,4}

In the present review, the data on the reagents for the synthesis and cleavage of 1,3-dithiolanes developed in the last decade are surveyed. The mechanisms of formation and cleavage of 1,3-dithiolanes are beyond the scope of this review.

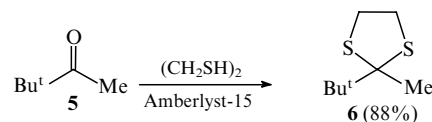
II. Reagents for the synthesis of 1,3-dithiolanes based on 1,2-ethanedithiol

1. Catalysis by Amberlyst-15

Amberlyst-15 is an efficient catalyst of the synthesis of 1,3-dithiolanes from some aldehydes,⁵ for example, from **1** or **2**, under the action of 1,2-ethanedithiol (CH_2SH)₂.



The reactions proceed at room temperature to form derivatives **3** or **4** in high yields. If the reaction mixtures contain ketones along with aldehydes, the former do not react with $(\text{CH}_2\text{SH})_2$ under these conditions. However, this procedure can also be used for protection of ketones (even sterically hindered ketones), if the reaction is carried out with boiling. Under these conditions, 1,3-dithiane **6** is formed from pinacolone **5**.



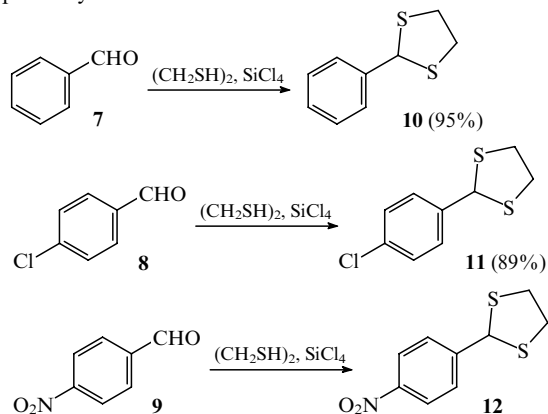
In this case, the workup procedure is substantially simpler than those used in the synthesis of 1,3-dithiolanes catalysed by other reagents, in particular, by thionyl chloride and impregnated silica gel,⁶ or in the synthesis of 1,3-dithianes from 2,2-dimethyl-1,3,2-dithiasilane in the presence of boron trifluoride etherate as a catalyst.⁷ Ketones of the type **5** react with $(\text{CH}_2\text{SH})_2$ in the presence of Amberlyst-15 to form dithiolane **6**. An important characteristic feature of this system is the fact that the reactions with ketones proceed at a slow rate because of which this procedure can be used for separation of aldehydes and ketones.

2. Catalysis by tetrachlorosilane

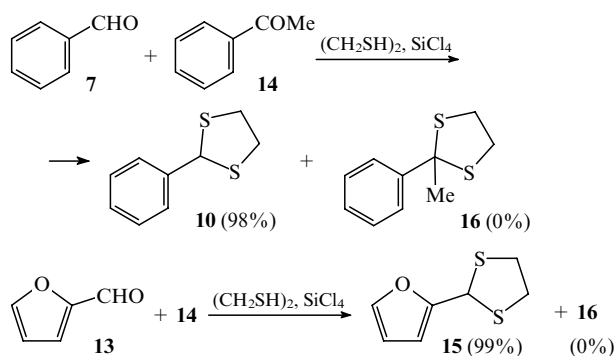
It is known⁸ that tetrachlorosilane (Lewis acid) is a soft and efficient catalyst of the synthesis of 1,3-dithiolanes. This compound catalyses the formation of dithiolanes from aromatic aldehydes containing both electron-donating and electron-with-

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drawing substituents. Thus the reactions of aldehydes **7–9** with $(\text{CH}_2\text{SH})_2$ in the presence of SiCl_4 afforded dithiolanes **10–12**, respectively.



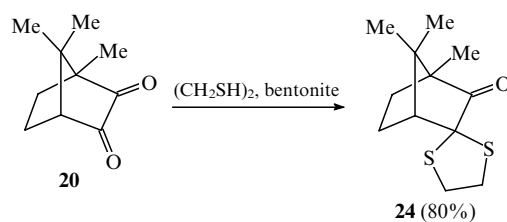
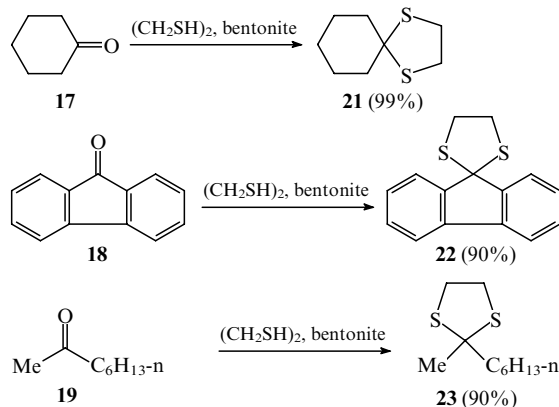
The SiCl_4 -catalysed reactions of aromatic aldehydes (for example, **7** and **13**) with $(\text{CH}_2\text{SH})_2$ in the presence of acetophenone (**14**) proceed absolutely chemoselectively to form the 1,3-dithiolanes **10** and **15**, respectively. Methyl-substituted dithiolane **16** is not formed in this reaction. Good selectivity is observed also in the case of aliphatic aldehydes.



Ku and Oh⁸ believed that the bulkiness and branching of the carbonyl compound are the major factors governing the chemoselectivity of formation of 1,3-dithiolanes.

3. Catalysis by bentonite

Miranda *et al.*⁹ developed an excellent procedure for the synthesis of 1,3-dithiolanes. This procedure involves condensation of ketones with $(\text{CH}_2\text{SH})_2$ in the presence of bentonite, which has also been used for the oxirane ring-opening¹⁰ and conversion of oximes into ketones.^{11, 12} Dithiolanes **21–24** were prepared in high yields from ketones **17–20**, respectively. The reactions were performed in anhydrous toluene in the presence of bentonite as a catalyst.



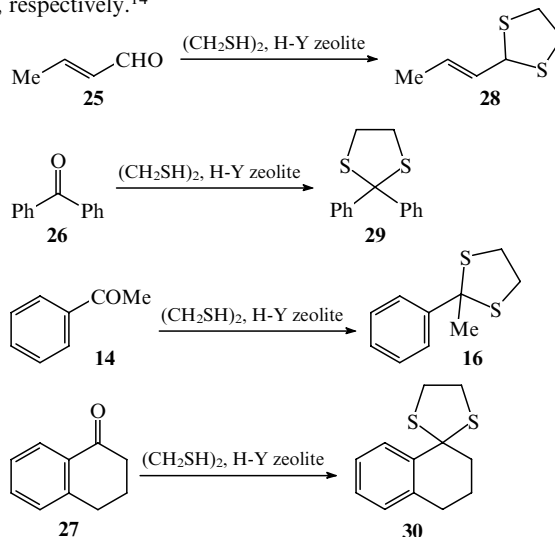
This procedure is very simple and bentonite is inexpensive. It should be noted that the amount of the catalyst required in this case is seven times smaller than the amount of montmorillonite KSF in analogous reactions and the crude reaction mixture gives only one spot on a thin-layer chromatogram.

4. Catalysis by anhydrous LaCl_3

Anhydrous LaCl_3 proved to be a convenient and efficient catalyst¹³ of conversions of the carbonyl compounds **7**, **9**, **13** and **17** under the action of $(\text{CH}_2\text{SH})_2$ into the dithiolanes **10**, **12**, **15** and **21**, respectively. The reactions proceeded smoothly giving the products in very high yields. Owing to mild conditions and the simplicity, this procedure is suitable for multistep syntheses of complex organic compounds. Hydrated rare-earth metal chlorides were ineffective for the preparation of 1,3-dithiolanes from some carbonyl compounds. Apparently, anhydrous salts adsorb water much more actively than the hydrates, which facilitates substitution in the intermediate hemithioacetal with elimination of a water molecule and coordination of the lanthanum ion at the oxygen atom of the carbonyl group resulting in an increase in the electrophilicity of the carbon atom.

5. Catalysis by H-Y zeolite

The reactions of crotonaldehyde (**25**) and aromatic and sterically hindered ketones **26**, **14** and **27** with $(\text{CH}_2\text{SH})_2$ in the presence of H-Y zeolite ($\text{Si} : \text{Al} = 2.43$) afforded 1,3-dithiolanes **28**, **29**, **16** and **30**, respectively.¹⁴



The use of H-ZSM-5 zeolite ($\text{Si} : \text{Al} = 45$) and H-mordenite has met with only limited success. The advantages of H-Y zeolite are the simplicity of separation, high yields of the products and the possibility of regeneration of the catalyst.

6. Catalysis by montmorillonite KSF

Montmorillonite KSF was used¹⁵ for conversions of some aldehydes, for example, of **7**, **9** and **31–33**, in the absence of solvents at room temperature to form 1,3-dithiolanes **10**, **12** and **34–36**, respectively.



7. Catalysis by $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$

8. Catalysis by bis(trimethylsilyl) sulfate adsorbed on silica gel

9. Catalysis by MgI_2 in diethyl ether

10. Catalysis by Dowex-50W-X8

Reaction 1: 4-methylbenzaldehyde (**43**) reacts with $(\text{CH}_2\text{SH})_2$ on Dowex-50W-X8 to form 4-methyl-2,5-dithiolane (**47**).

 Reaction 2: 2,3-benzodioxymethanal (**44**) reacts with $(\text{CH}_2\text{SH})_2$ on Dowex-50W-X8 to form 2,3-benzodioxo-2,5-dithiolane (**48**).

 Reaction 3: 1,2,3,4-tetrahydronaphthalen-1-one (**45**) reacts with $(\text{CH}_2\text{SH})_2$ on Dowex-50W-X8 to form 1,2,3,4-tetrahydro-1,4-dithianaphthalene (**49**).

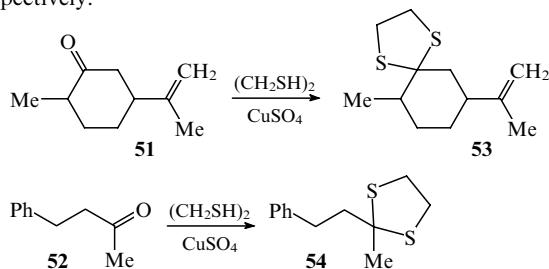
 Reaction 4: 1,2,3,4,5,6-hexahydro-1H-cyclohepta[1,2-b]pyridine-1-one (**46**) reacts with $(\text{CH}_2\text{SH})_2$ on Dowex-50W-X8 to form 1,2,3,4,5,6-hexahydro-1,4-dithianocyclohepta[1,2-b]pyridine (**50**).

Apparently, resin Dowex-50W-X8 treated with HCl acts as an acidic catalyst and increases the electrophilicity of the carbon atom of the carbonyl group. In the presence of this catalyst, the sterically hindered aromatic ketones **14** and **26** are smoothly converted into the dithiolanes **16** and **29**, respectively. This

method can also be used in the case of compounds containing acid-sensitive groups. The reactions are completed in a short time.

11. Catalysis by CuSO₄

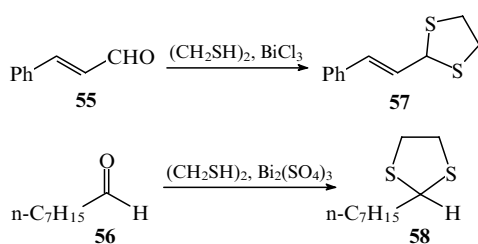
The reactions of some carbonyl compounds, for example, of α -tetralone (27), 5 α -cholestan-3-one (37), dihydrocarvone (51), 4-phenylbutan-2-one (52), acetophenone (14) and benzophenone (26), with 1,2-ethanedithiol in dry THF in the presence of anhydrous copper sulfate, which is a gentle and inexpensive catalyst, afforded the thiolanes 30, 40, 53, 54, 16 and 29, respectively.²⁰



The reactions catalysed by $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ afford dithiolanes in very low yields. The advantage of this method is the fact that it can be applied in the case of various aliphatic, aromatic and steroid ketones.

12. Catalysis by bismuth halides and sulfate

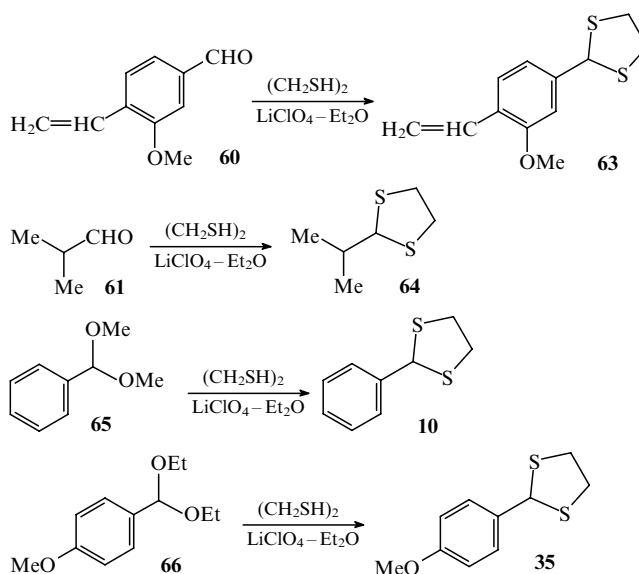
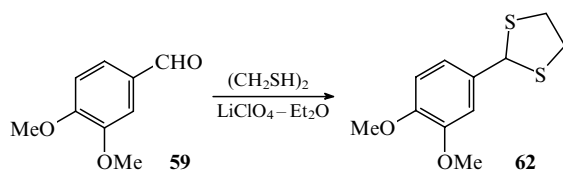
Bismuth halides BiX_3 ($\text{X} = \text{Cl}, \text{Br}$ or I) and bismuth sulfate $\text{Bi}_2(\text{SO}_4)_3$ in acetone are powerful catalysts²¹ of conversions of carbonyl compounds, for example, of 8, 14, 55 and 56, under the action of $(\text{CH}_2\text{SH})_2$ at room temperature giving rise to the dithiolanes 11, 16, 57 and 58, respectively.



These bismuth salts offer the following advantages over various Lewis and Brønsted acids: (1) minimum amounts of these salts are required; (2) the salts exhibit catalytic activities under mild conditions; (3) the synthetic procedure is simple; (4) the products are prepared in high yields; (5) the reactions are chemoselective; (6) the catalyst is inexpensive and nontoxic; (7) it is possible to recognise the type of the carbonyl functional group. The high activity of this catalyst is retained in the presence of a small amount of water. An acid-sensitive substrate, such as furfural (13), is readily converted into dithiolane without self-condensation and ring opening.

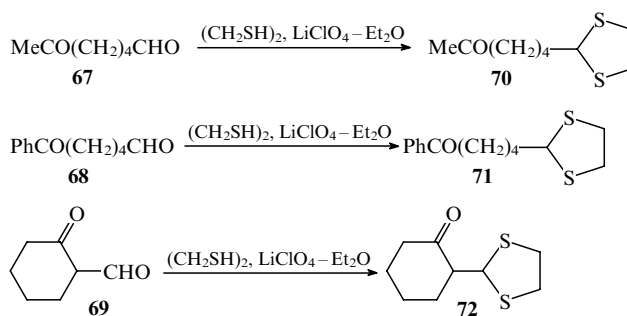
13. Catalysis by lithium perchlorate in diethyl ether

The reactions of aldehydes 59–61 with $(\text{CH}_2\text{SH})_2$ yielding dithiolanes 62–64, respectively, are catalysed by lithium perchlorate in diethyl ether.²² Analogously, acetals 65 and 66 are converted into the dithiolanes 10 and 35, respectively.



These reactions proceed at room temperature to form 1,3-dithiolanes in high yields.[†] It appeared that ketones and their acetals react much more slowly than aldehydes and their acetals.

Yet another advantage of the above-mentioned system is its ability to perform chemoselective thioacetalisation of oxoaldehydes 31 and 67–69 in the synthesis of dithiolanes 34 and 70–72, respectively.



In this case, the aldehyde carbonyl group is selectively protected, while the keto group remains intact. The selectivity is absent in the reactions performed with the use of such Lewis acids as BF_3 or AlCl_3 .

14. Catalysis by ammonium cerium nitrate

Some aldehydes, for example, 7, 25, 59 and 61, were converted into dithiolanes 10, 28, 62 and 64, respectively, under the action of $(\text{CH}_2\text{SH})_2$ catalysed by $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$.²⁴ These dithiolanes were prepared in high yields at room temperature. In the presence of ketones, only aldehydes enter into the reactions. The reaction conditions and the synthetic procedure are very simple and convenient. This procedure can be extended to ketones. For example, cyclohexanone (17) gave the dithiolane 21 upon refluxing in chloroform for 10 h. It should be noted that aromatic ketones, γ -lactones and acyclic ketones do not react under the above-mentioned conditions, and hence, this catalyst is convenient for chemoselective thioacetalisation. Ammonium cerium nitrate is comparable in efficiency with the above-described solution of lithium perchlorate in diethyl ether.²²

[†] It should be noted that the reaction of dimethyl acetal 65 with 1,2-ethanedithiol in the presence of TeCl_4 in dichloromethane affords the dithiolane 10 in 99% yield.²³

15. Catalysis by zirconium(IV) chloride adsorbed on silica gel

The dithiolanes **10**, **16**, **21**, **22**, **29** and **57** are formed in high yields by the reactions of the carbonyl compounds **7**, **14**, **17**, **18**, **26** and **55**, respectively, with 1,2-ethanedithiol in the presence of ZrCl_4 adsorbed on silica gel.²⁵ This method has the following advantages: (1) the procedure is simple and convenient; (2) the reactions proceed smoothly; (3) the reactions are rapid and the system can be used in the case of low-reactivity ketones, such as **26** and **14**. Thioacetalisation of α,β -unsaturated aldehydes, for example, of cinnamaldehyde (**55**), can be performed with excellent yield, but attempts to prepare dithiolanes from α,β -unsaturated ketones in good yields were unsuccessful.

16. Catalysis by natural kaolin

Recently, it has been demonstrated²⁶ that kaolin efficiently catalyses conversions of the carbonyl group into the dithiolane moiety, for example, in the reactions of the compounds **7**, **13**, **26** and **55** with $(\text{CH}_2\text{SH})_2$ giving rise to the 1,3-dithiolanes **10**, **15**, **29** and **57**, respectively. It was also noted that the reaction of a mixture of benzaldehyde (**7**) and acetophenone (**14**) with 1,2-ethanedithiol in the presence of 10% of kaolin afforded only the dithiolane **10**, while acetophenone remained unconsumed.

Owing to high chemoselectivity, the reactions catalysed by kaolin may be advantageous in the selective protection of aldehydes in the presence of other carbonyl compounds.

17. Catalysis by LiBr

Aldehydes, for example, **7** and **55**, are converted into the dithiolanes **10** and **57**, respectively, in high yields under the action of $(\text{CH}_2\text{SH})_2$ without a solvent in the presence of catalytic amounts of lithium bromide.²⁷ Under similar conditions, the aromatic and aliphatic ketones **14** and **61** do not react even over several hours. This procedure is unsuitable for the preparation of dithiolanes in such solvents as THF and dichloromethane. In the latter solvents, aldehydes remain unconsumed. Due to the neutrality of the reaction medium, the procedure under consideration is very useful in the case of substrates highly sensitive to acids. The excellent selectivity and simplicity allow one to use this method successfully for selective conversions of aromatic and α,β -unsaturated aldehydes containing other carbonyl groups into 1,3-dithiolanes under very mild conditions.

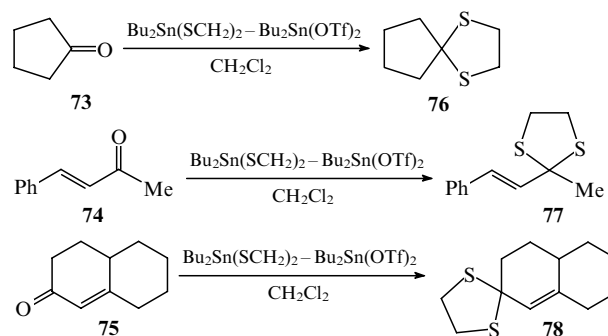
18. Catalysis by copper(II) trifluoromethanesulfonate adsorbed on silica gel

A large number of aldehydes and ketones, for example, **7**, **8**, **14**, **26**, **32** and **43**, were converted into 1,3-dithiolanes by reactions with $(\text{CH}_2\text{SH})_2$ in the absence of a solvent and in the presence of catalytic amounts of copper(II) trifluoromethanesulfonate $\text{Cu}(\text{OTf})_2$ adsorbed on silica gel.²⁸ Analogous conversions are catalysed by $\text{Cu}(\text{OTf})_2$ in dichloromethane. Aldehydes react more rapidly than ketones. The reactions with aldehydes and ketones proceed chemoselectively, *viz.*, primarily aldehydes are involved in the reactions. In most cases, the reactions proceed smoothly. Such a sterically hindered and low-reactivity ketone as benzophenone (**26**) is inert with respect to the system under consideration without a solvent at room temperature, but the reaction proceeds in toluene on heating to 80 °C. Conversions of some aldehydes and ketones into 1,3-dithiolanes without a solvent were also observed in the presence of catalytic amounts of copper chloride adsorbed on silica gel, but the reactions proceeded slowly with low yields. The procedure for thioacetalisation of carbonyl compounds without a solvent may find wide use in organic synthesis in the future.

19. Catalysis by dibutyl(ethylenedithio)stannane in the presence of $\text{Bu}_2\text{Sn}(\text{OTf})_2$

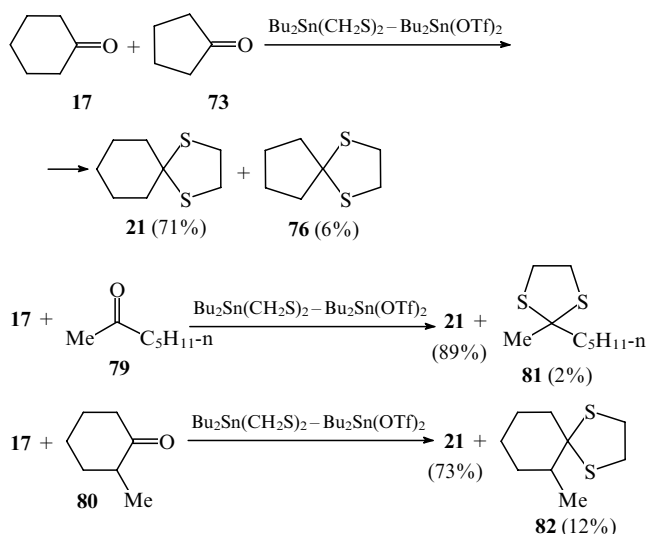
Sato *et al.*²⁹ reported the conversions of the ketones **17** and **73–75** into the dithiolanes **21** and **76–78**, respectively, upon treatment

with dibutyl(ethylenedithio)stannane $\text{Bu}_2\text{Sn}(\text{SCH}_2)_2$ in the presence of $\text{Bu}_2\text{Sn}(\text{OTf})_2$ in dichloromethane.



This procedure for the synthesis of dithiolanes is to some extent comparable with that proposed by Evans *et al.*³⁰ The latter procedure involves thiosilanes and has been used only for carbonyl compounds. An important advantage of the procedure under consideration is the simplicity of the synthesis of thiostannane from various organotin compounds. In addition, thiostannane is air- and moisture-stable and can be stored in air. The procedure with the use of thiostannane and organotin triflate may be useful in preparing dithiolanes not only from ketones but also from their ketals.

Organotin triflates can be used for separation of ketones (or their ketals). If the reaction mixtures contain cyclopentanone (**73**), heptan-2-one (**79**) or 2-methylcyclohexanone (**80**) along with cyclohexanone (**17**), the reactions proceed primarily with cyclohexanone. The yield of the dithiolane **21** is very high compared to the yields of the compounds **76**, **81** and **82**.



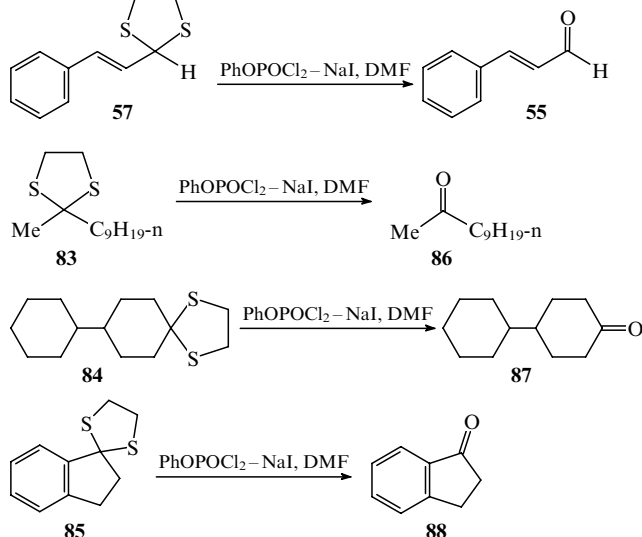
This high selectivity cannot be achieved by conventional methods, for example, with the use of $(\text{CH}_2\text{SH})_2$ and $\text{BF}_3 \cdot \text{OEt}_2$. This possibility of separation is of great importance in the chemistry of steroids.

III. Reagents for the cleavage of 1,3-dithiolanes

A large number of procedures were developed for conversions of dithiolanes into the initial carbonyl compounds.^{1,31} Some of them require drastic conditions or the use of toxic compounds, for example, mercury salts. In some cases, dithiolanes are decomposed under mild conditions in several steps. In this connection, a demand arose for the development of new procedures for deprotection of dithiolanes and construction of new reagents which do not affect other functional groups.

1. The phenyl phosphorodichloridate–sodium iodide system in DMF

Liu and Wiszniewski³² used phenyl phosphorodichloridate in combination with sodium iodide in DMF for conversions of dithiolanes, for example, of **57** and **83–85**, into the corresponding carbonyl compounds **55** and **86–88**.

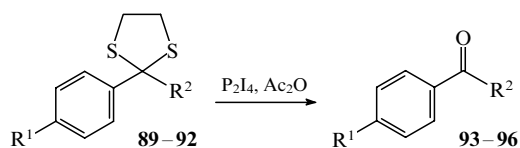


Ketones are formed in high yields. The reactions can be performed at room temperature. In the reactions with the use of acetonitrile instead of DMF, dithiolanes are recovered. The reactions carried out with boiling afford mixtures of products.

This procedure³² is applicable to aliphatic, aromatic and allylic dithiolanes. In all cases, the reactions proceed smoothly yielding the only desired product, which was confirmed by TLC data.

2. Phosphorus tetraiodide in acetic anhydride

Shigemasa *et al.*³³ developed a procedure for decomposition of 1,3-dithiolanes, for example, of **89–92**, under the action of P₂I₄ in acetic anhydride, chloroform or CCl₄ giving rise to ketones **93–96**, respectively, in high yields.

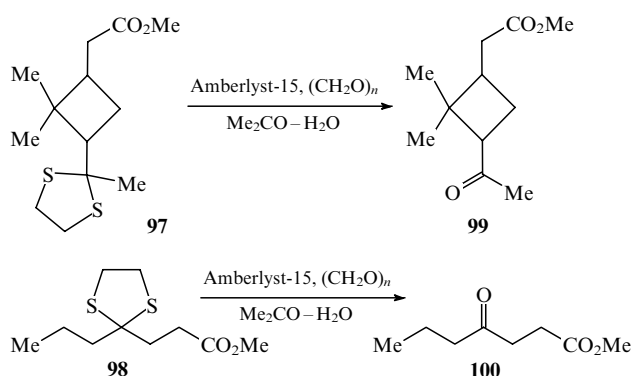


Dithiolane	Ketone	R ¹	R ²
89	93	MeO	Ph
90	94	Me	Ph
91	95	Cl	Ph
92	96	MeO	Bu ⁿ

The reactions of these 1,3-dithiolanes with P₂I₄ in dichloromethane result primarily in reductive desulfurisation and partial deprotection. In all cases, the amount of the reduced product is substantially higher than the amount of the ketone formed.

3. Amberlyst-15–paraformaldehyde in wet acetone

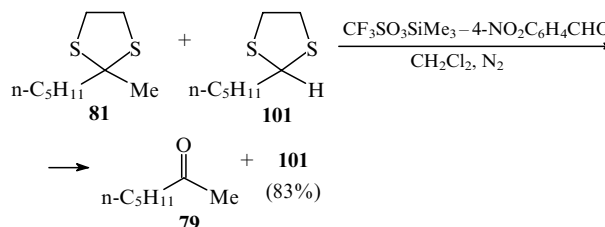
The dithiolanes **10**, **22**, **35**, **97** and **98** were converted into the ketones **7**, **18**, **33**, **99** and **100**, respectively, under the action of Amberlyst-15 and paraformaldehyde.³⁴



The dithiolanes were dissolved in aqueous acetone. Then paraformaldehyde and Amberlyst-15 were added and the reaction mixture was heated at 80 °C for 15–20 h. In these reactions, acid-sensitive ethers and esters remain intact.

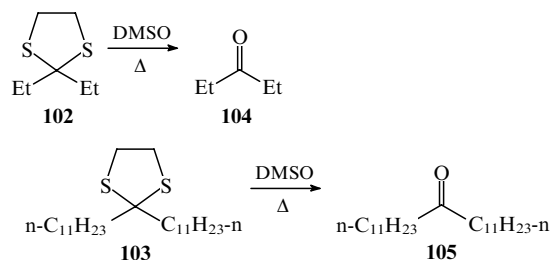
4. Trimethylsilyl trifluoromethanesulfonate–4-nitrobenzaldehyde in CH₂Cl₂

A new procedure for the cleavage of dithiolanes³⁵ involves the addition of CF₃SO₃SiMe₃ to a mixture of dithiolane and 4-nitrobenzaldehyde in dichloromethane at room temperature. This procedure was used for conversions of the dithiolanes **16**, **30**, **35** and **57** into the ketones and aldehydes **14**, **27**, **32** and **55**, respectively. The reactions can be performed with the use of CF₃SO₃SiBu^tMe₂ instead of CF₃SO₃SiMe₃. Of the four aldehydes tested in the study,³⁵ 4-nitrobenzaldehyde was chosen because this reagent made it possible to accelerate the reaction and to improve the efficiency of migration of the sulfur. This method can also be used for selective deprotection of dithiolanes prepared from ketones in the presence of dithiolanes obtained from aldehydes. Thus 1,3-dithiolane **81** was hydrolysed to give ketone **79** in the presence of compound **101**. This is the first example of catalytic transthioacetalisation with simultaneous migration of oxygen and alkanethiol proceeding irreversibly in an anhydrous medium.



5. Dimethyl sulfoxide, 140–160 °C

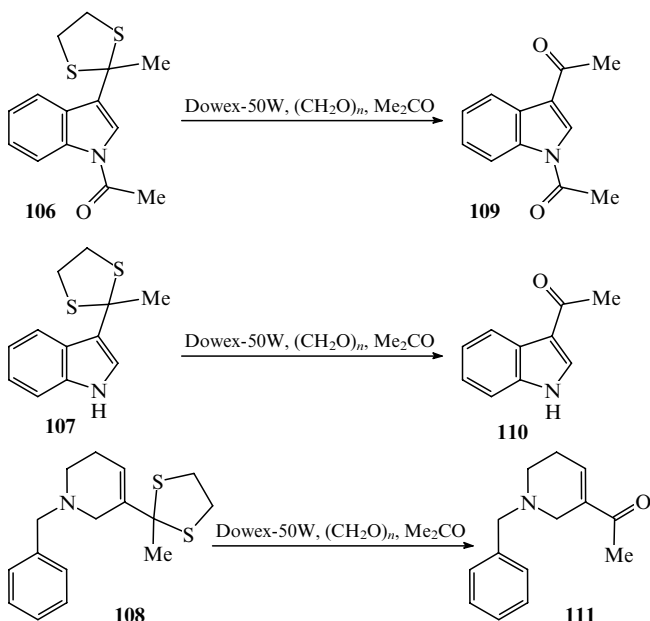
In the absence of other reagents, DMSO catalyses³⁶ cleavage of some dithiolanes, for example, of **30**, **57**, **102** and **103**, at high temperature giving rise to the corresponding carbonyl compounds **27**, **55**, **104** and **105** in high yields.



It is known that DMSO can decompose dithiolanes in the presence of iodine³⁷ or *tert*-butyl chloride.³⁸

6. Dowex-50W – paraformaldehyde in acetone

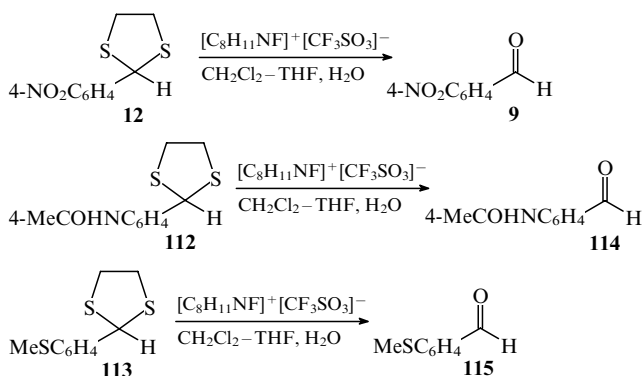
Giri and Sankar³⁹ used a mixture of the acidic catalyst Dowex-50W and paraformaldehyde in acetone for the cleavage of dithiolanes of nitrogen-containing heterocyclic compounds **106–108** to yield ketones **109–111**, respectively.



Although the cleavage of such dithiolanes is generally performed with the use of mercury salts, the latter sometimes form insoluble complexes. This difficulty was overcome⁴⁰ by protection of the nitrogen atom before hydrolysis of dithiolanes with triethyloxonium tetrafluoroborate. Taking into account the simplicity of the procedure and the good yield of the product, we believe that this procedure³⁹ is superior in efficiency to all other available procedures for dethioacetalisation of nitrogen-containing heterocycles.

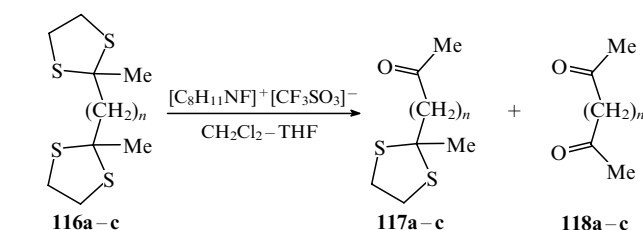
7. *N*-Fluoro-2,4,6-trimethylpyridinium triflate in a 1 : 1 CH_2Cl_2 – THF mixture and H_2O

Dithiolanes **12**, **112** and **113** were decomposed to aldehydes **9**, **114** and **115**, respectively, with the use of *N*-fluoro-2,4,6-trimethylpyridinium triflate $[\text{C}_8\text{H}_{11}\text{NF}]^+[\text{CF}_3\text{SO}_3]^-$ in a 1 : 1 CH_2Cl_2 – THF mixture and 5 equiv. of H_2O .⁴¹ High yields of compounds **9**, **114** and **115** were achieved by performing the reactions under an inert atmosphere (Ar or N_2). The reactions performed in the presence of oxygen or nitrobenzene give rise to a number of unidentified by-products. The reactions in pure dichloromethane, ether, hexane or acetonitrile as the solvent afford aldehydes in low yields. In DMF, dithiolanes do not decompose.



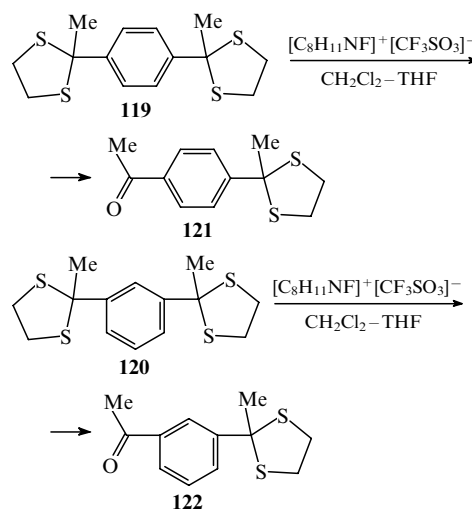
In the reactions of the title reagent with dithiolanes **116a–c**, the latter decompose to form mono- and diketones. The ratio between the monoketones **117a–c** and the diketones **118a–c**

prepared from the thioacetals **116a–c** decreases as the length of the carbon chain separating two dithiolane groups increases.



Compound	<i>n</i>	Yield (%)	
116–118		117	118
a	0	74	5
b	1	57	15
c	2	52	21

The cleavage of dithiolanes of aromatic derivatives **119** and **120** with *N*-fluoro-2,4,6-trimethylpyridinium triflate in the presence of water also afforded predominantly monoketones. The higher selectivity of the formation of *para*-substituted **121** ketone compared to the *meta*-isomer **122** is indicative of the important role of electronic effects and agrees with the cationic nature of intermediates.



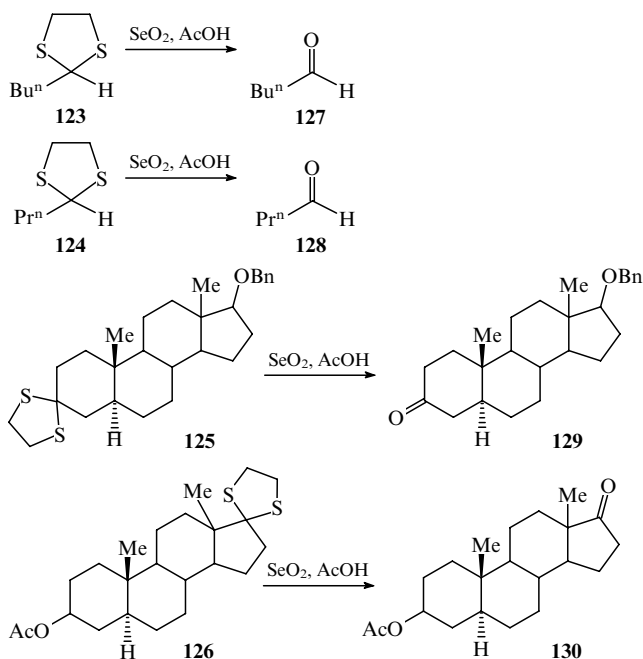
Finally, it should be noted that hydrolysis of dithiolanes with a mixture of *N*-fluoro-2,4,6-trimethylpyridinium triflate and water was not accompanied by migration of the electrophilic fluorine atom. This fact is in contradiction with the mechanism of fluorination of organic substrates with *N*-fluoropyridinium cations proposed previously.⁴²

8. Copper(II) chloride – silica gel in CH_2Cl_2

The dithiolanes **16**, **40**, **53** and **54** were decomposed under the action of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ adsorbed on silica gel under mild conditions to form the corresponding carbonyl compounds **14**, **37**, **51** and **52**.²² The yields of the products obtained with the use of dichloromethane are substantially higher than those obtained with the use of THF. The reagent under consideration can be successfully used for the cleavage of dithiolanes of various aliphatic, aromatic and sterically hindered steroid compounds. The reaction conditions are very simple and convenient.

9. Selenium dioxide in acetic acid

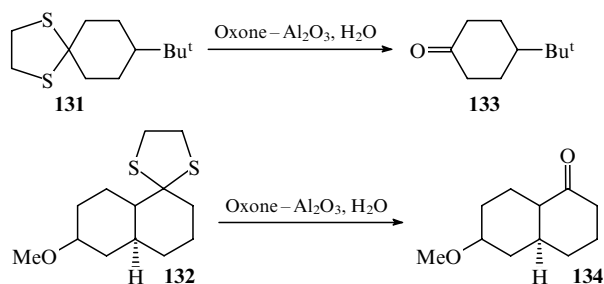
A solution of SeO_2 in acetic acid proved to be an efficient reagent for the deprotection of 1,3-dithiolanes **123–126** to yield the aldehydes and ketones **127–130**, respectively.⁴³



The reactions proceed readily at room temperature giving rise to carbonyl compounds in very high yields. Widespread functional groups, such as ethers and esters, do not react with selenium dioxide. This procedure is very useful in the case of dithiolane derivatives of C(7)- and C(13)-steroid ketones whose cleavage generally requires drastic conditions. The presence of acetic acid is of importance because the reactions in aprotic solvents, for example, in THF, dichloromethane or toluene, proceed with very low yields. Hydrolysis in aqueous acetonitrile or acetone proceeds slowly (20–30 h) and affords cleavage products in low yields. Heating of the mixture accelerates the reaction, but the yield becomes even lower because a number of undesirable products are formed. The best results of the cleavage of dithiolanes and the highest yields of ketones regenerated are achieved with the 1,3-dithiolane to SeO_2 ratio of 1 : 5. On the whole, the procedure proposed for hydrolysis of 1,3-dithiolanes is rapid and convenient, characterised by high yields and is applicable to various compounds.

10. Oxone – wet Al_2O_3

Dithiolanes **30**, **131** and **132** were converted into ketones **27**, **133** and **134**, respectively, in high yields under mild conditions with the use of Oxone (potassium hydrogen persulfate, $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$) and wet alumina.⁴⁴



The carbonyl compounds were obtained in high yields by refluxing 1,3-dithiolanes in chloroform in the presence of Oxone on Al_2O_3 , the functional groups, such as ethers and esters, and double bonds remaining intact. The procedure is simple and convenient, which is an additional advantage of this reagent for dethioacetalisation. This procedure is comparable in efficiency

with the above-described procedures for hydrolysis of dithiolanes or even superior to these methods.

11. Iron(III) nitrate – montmorillonite K10 – hexane

Hirano *et al.*⁴⁵ developed an efficient and simple procedure for oxidative cleavage of 1,3-dithiolanes with the use of iron(III) nitrate and montmorillonite K10 in hexane at 50 °C. This procedure was used for conversions of the 1,3-dithiolanes **12**, **57** and **89–92** into the carbonyl compounds **9**, **55** and **93–96**, respectively, in very high yields. In the absence of the clay, the reactions proceed slowly and afford ketones in lower yields. The advantages of this system over other supported reagents, such as iron(III) or copper(II) nitrates on montmorillonite K10 in the absence of hexane⁴⁶ or copper(II) nitrate on silica gel,⁴⁷ are the high reaction rate and the fact that there is no need for pretreatment of the reagent. Therefore, this procedure is an improved modification of the above-described methods. Hexane is a better solvent from economic and environmental standpoints compared to chlorinated hydrocarbons (CH_2Cl_2 , CHCl_3 and CCl_4), which are often used in standard heterogeneous systems. On the whole, this procedure for the cleavage of 1,3-dithiolanes and regeneration of carbonyl compounds is simple and convenient and satisfies economic requirements.

12. Zirconium sulfophenylphosphonate

Mixed zirconium(IV) methylphosphonate sulfophenylphosphonate, $\text{Zr}(\text{O}_3\text{PCH}_3)_{1.2}(\text{O}_3\text{PC}_6\text{H}_4\text{SO}_3\text{H})_{0.8}$, proved to be a very useful catalyst⁴⁸ for mild hydrolysis of 1,3-dithiolanes to form the corresponding carbonyl compounds. Dithiolanes are heated with a catalyst in the presence of glyoxylic acid monohydrate as an exchange reagent. This procedure was used for the preparation of the carbonyl compounds **7**, **14**, **37** and **133** from the dithiolanes **10**, **16**, **40** and **131**, respectively, in very high yields. Zirconium sulfophenylphosphonate is also a very efficient catalyst of the cleavage of cyclic dithioacetal, which is resistant to a number of other reagents.⁴⁹ It is noteworthy that zirconium sulfophenylphosphonate is comparable in activity with the above-described reagents or even superior to them. The essential advantages of this procedure are the absence of the solvent, mild conditions and the simplicity.

13. Miscellaneous procedures

The major reagents and catalysts used for the deprotection of 1,3-dithiolanes were considered in the previous sections. In addition, some dithiolanes were decomposed with the use of systems based on silver nitrate,⁵⁰ bis(trifluoroacetoxy)iodobenzene,⁵¹ nitrogen oxides,⁵² visible light⁵³ and tantalum chloride.⁵⁴ Since these procedures were rarely used, we do not consider them in detail in the present review.

IV. Conclusion

The problem of protection of the carbonyl groups in aldehydes and ketones, in particular, the protection giving rise to 1,3-dithiolanes, is of great importance in organic synthesis due to which an array of procedures for the introduction of this group were developed. The most frequently used methods were considered above. It should be noted that a large number of reagents for subsequent cleavage of 1,3-dithiolanes and regeneration of carbonyl-containing compounds have been proposed in recent years. Apparently, new reagents for introduction and removal of the dithiolane group will be developed in the future. In our opinion, the dithiolane moiety should be more extensively used as a protective group. We hope the present review will help to attract the attention of chemists engaged in organic chemistry to this problem.

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Polynuclear complexes of copper(I) halides: coordination chemistry and catalytic transformations of alkynes

B M Mykhalichko, O N Temkin, M G Mys'kiv

Contents

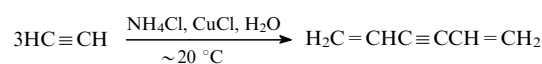
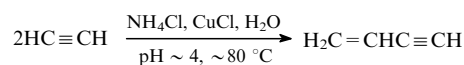
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Abstract. Characteristic features of the coordination chemistry of Cu(I) and mechanisms of catalytic conversions of alkynes in the $\text{CuCl}-\text{MCl}-\text{H}_2\text{O}-\text{HC}\equiv\text{CR}$ system (MCl is alkali metal or ammonium chloride or amine hydrochloride; $\text{R} = \text{H}, \text{CH}_2\text{OH}, \text{CH}=\text{CH}_2$, etc.) are analysed based on studies of the compositions and structures of copper(I) chloride (bromide) complexes, alkyne π -complexes and ethynyl organometallic polynuclear compounds formed in this system in solutions and in the crystalline state. The role of polynuclear complexes in various reactions of alkynes is discussed. The bibliography includes 149 references.

I. Introduction

Copper(I) complexes occupy a significant place in the chemistry of coordination compounds and in the development and evolution of homogeneous metal-complex catalysis. Copper(I) salts in quinoline were the first catalysts used in homogeneous hydrogenation.^{1,2} Copper(I) chloride was among the first commercial homogeneous metal-complex catalysts (dimerisation of acetylene).^{3,4} Acetylenic complexes of copper(I) were prepared for the first time by Chavastelon as early as 1898 in studies of the reactions of CuCl with C_2H_2 in aqueous solutions of KCl.^{5,6} The compositions $2\text{KCl}\cdot 8\text{CuCl}\cdot \text{C}_2\text{H}_2$, $\text{KCl}\cdot 4\text{CuCl}\cdot \text{C}_2\text{H}_2$, $\text{KCl}\cdot 2\text{CuCl}\cdot \text{C}_2\text{H}_2$ and $2\text{CuCl}\cdot \text{C}_2\text{H}_2$ were assigned to the crystalline adducts isolated.^{5–7} However, interest in the reactions of acetylene with CuCl and in catalysis by copper(I) complexes has particularly increased^{3,4,8,9} after brilliant studies on catalysis of dimerisation and hydrochlorination of acetylene by copper(I) chloride complexes performed by Nieuwland^{3,10} and the development of the commercial synthesis of chloroprene and synthetic rubber neoprene by Carothers (Du Pont de Nemours; see the monograph³). Thus, Nieuwland and coworkers¹⁰ (in 1929–1931) were the first to perform the catalytic synthesis of linear oligomers of C_2H_2 by the reaction of a concentrated solution of NH_4Cl and

CuCl in water (the molar ratio $\text{NH}_4\text{Cl}:\text{CuCl}:\text{H}_2\text{O} = 2:3:7$) with acetylene.



Conversions of acetylene in these systems are accompanied by a sharp decrease in pH of the medium (from ~ 4 to 1.1 at 80°C). Alkali metal chlorides¹¹ or amine hydrochlorides (hereinafter, MCl)¹² can be used instead of NH_4Cl as a component of the catalytic Nieuwland system. Concentrated solutions of MCl and CuCl proved to be also very efficient catalysts of other catalytic reactions of acetylene (for example, the addition of H_2O , HCl, HCN, RSH and C_5H_6 ; see Refs 1 and 13), dienes and dichlorobutenes.¹⁴

The major proposals for the mechanisms of various reactions of alkynes catalysed by copper(I) chloride complexes, including oxidation processes with the participation of the Cu(I)–Cu(II) system, were developed in 1960–1990.^{13,14} Certain specific features of copper(I) halide complexes are of most interest in their coordination chemistry and catalysis, among which are the pronounced tendency to form polynuclear complexes and, consequently, the possibility of the occurrence of multielectron processes, the formation of polynuclear π -complexes and σ -organometallic compounds with μ_2 - and μ_3 -bridging groups, the formation of heterovalent polynuclear complexes¹⁵ and the ability to activate alkynes, alkenes and dienes in various addition, substitution and oxidation reactions.

The distinguishing feature of concentrated solutions of MCl and CuCl in water is the formation of a large number of polynuclear $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ complexes, which can participate to a variable extent in the same catalytic process and react with acetylene and its derivatives giving rise to intermediate π - and σ -complexes with different compositions and structures and of different nature. The understanding of the mechanism of catalytic reactions depends substantially on the available information on the structures of possible intermediates. Until recently, investigations of these intermediates were restricted to isolation of adducts and determination of their chemical compositions. During the last 15 years, a series of studies has been aimed at synthesising copper-containing complexes both of chloride (inorganic) and π - and σ -organocopper compounds and establishing their crystal structures.^{16–19}

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In this review, the data on the coordination chemistry, synthesis and structures of complex compounds of CuCl (CuBr) with acetylene and its derivatives and on catalysis with the participation of copper(I) chloride (bromide) complexes and alkynes are generalised and systematised and the possible mechanisms of oligomerisation of acetylene and other processes catalysed by copper complexes are discussed. In this connection, particular attention will be given to catalytic reactions of acetylene and its derivatives proceeding in highly concentrated aqueous solutions of MCl and CuCl because it is in these homogeneous systems that copper(I) chloride complexes exhibit the highest catalytic activity.¹³

Researchers from the former Soviet Union and the Community of Independent States (primarily, from Russia and Ukraine) have made a significant contribution to these investigations. In the present review, these studies are considered in detail.

II. Complexes of copper(I) halides in solutions and in the crystalline state

Systems of copper(I) chloride with aqueous solutions of alkali metal chlorides, ammonium chloride or amine hydrochlorides are of such great interest that studies of the state of copper in these solutions and mechanisms of their catalytic reactions, which were started late in the 19th century, are being continued. Investigations of the solubility⁸ and other physicochemical properties of concentrated solutions of MCl and CuCl in water and isolation of the products obtained in the reaction of acetylene with CuCl, which incorporate one, two, three or even six CuCl molecules per C₂H₂ molecule,^{4, 7, 11, 20} provided evidence that these solutions contained polynuclear complexes with composition (Cu_mCl_n)^{(n-m)-}.

1. Physicochemical properties of concentrated MCl–CuCl–H₂O solutions

The abundant data on the solubility of CuCl in aqueous solutions of MCl have been reported in a monograph.⁴ The NH₄Cl–CuCl–H₂O system has been studied extensively.^{21, 22} The solubility of CuCl increases sharply as the concentration of NH₄Cl increases and the mole fraction of water decreases (Figs 1 and 2). The [CuCl]:[NH₄Cl] ratio is noticeably larger than unity at 80 and 100 °C, which is indicative of the formation of polynuclear copper(I) chloride complexes. This is also evident from calculations of the Bjerrum formation function $\tilde{n}$ (or the Sillén function *Z*) based on the results of the potentiometric determination of the equilibrium concentration of the ligand ([Cl]⁻):

$$\tilde{n} = \frac{[\text{Cl}^-]_{\Sigma} - [\text{Cl}^-]}{[\text{CuCl}]_{\Sigma}}$$

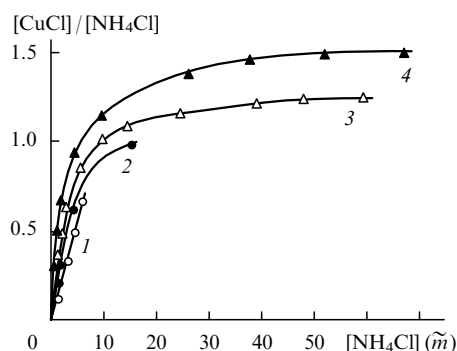


Figure 1. Dependence of the [CuCl]/[NH₄Cl] molar ratio on the molal concentration of NH₄Cl at different temperatures.²¹ *T* (°C): (1) 25; (2) 50; (3) 80; (4) 100.

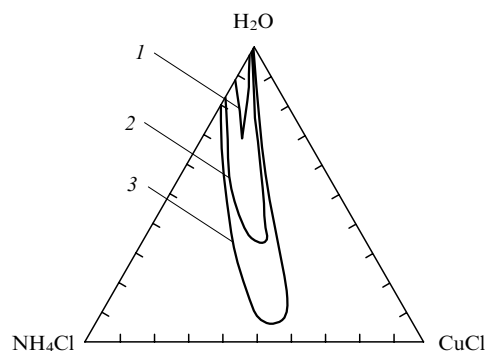


Figure 2. Triangular phase diagram of the solubility of CuCl (mole fractions).²¹ *T* (°C): (1) 25; (2) 80; (3) 100.

At the overall concentration of NH₄Cl and NH₄NO₃ of 10 $\tilde{m}$ ($\tilde{m}$ is the molal concentration), the $\tilde{n}$ value changes from 2.80 to 1.73 as the concentration of CuCl changes from 0.5 to 10 $\tilde{m}$ and the concentration of NH₄Cl changes from 1.5 to 10 $\tilde{m}$ (80 °C). The dependence of $\tilde{n}$ on [CuCl] also indicates the existence of polynuclear complexes.²²

Dissolution of CuCl in solutions of NH₄Cl is a slightly endothermic process (ΔH^0 changes from 16.7 to 4.18 kJ mol⁻¹ as the concentration of NH₄Cl changes from 1.5 to 15 $\tilde{m}$) and is accompanied by an increase in the entropy (ΔS_{298}^0 changes from 36 to 45 J mol⁻¹ K⁻¹).^{21, 23} Dissolution of CuCl is accompanied by dehydration of chloride ions resulting in an increase in *p*_{H₂O} and the activity of water (*a*_{H₂O}).²³ In the range of CuCl concentrations from 0 to 10 $\tilde{m}$ ([NH₄Cl] = 8.84 $\tilde{m}$), the *a*_{H₂O} value increases from ~ 0.74 to 0.83 (55 °C) and 0.88 (85 °C).



Studies of concentrated solutions of copper(I) chloride in NH₄Cl by electronic spectroscopy²⁴ (λ_{max} were 200, 235 and 273–400 nm) demonstrated that these solutions contain two groups of complexes because the optical density of the solution increases in the region of 250–290 nm and decreases in the region of 340–370 nm as the concentration of NH₄Cl increases. The absorption band in the region of 340–370 nm is the sum of absorption bands of different polynuclear complexes.

A comparison of the absorption spectra of chloride and bromide complexes in solutions in KX (5 $\tilde{m}$, X = Cl or Br) in the regions of 273 and 300–330 nm at the CuX concentrations of 0.01 and 0.4 $\tilde{m}$ demonstrated²² that the shifts of the absorption maxima to the long-wavelength region are no larger than 5–8 nm on going from Cl⁻ to Br⁻. It was assumed^{24, 25} that the longer-wavelength bands ($\lambda \simeq 320$ nm, $\epsilon_{\text{Br}^-} \simeq 150$) belong to the forbidden transitions $3d^{10} \rightarrow 3d^9 4s^1$ and the bands at 200 and 273 nm belong to the transitions $3d^{10} \rightarrow 3d^9 4p^1$.

2. Complexation equilibria in the MCl–CuCl–H₂O and NH₄Cl–CuCl–H₂O catalytic systems

The equilibria of the formation of copper(I) chloride complexes in rather dilute solutions have been studied in detail.²⁶ The concentration stability constants ($\beta_{m,n}$) for the complexes (Cu_mCl_n)^{(n-m)-} in the NaClO₄–NaCl–HCl–CuCl system with an ionic strength of the solution *I* = 5 mol litre⁻¹ and [HCl] = 0.1 mol litre⁻¹ (25 °C) were determined by two methods. The potentiometric method was used for [NaCl] = 0.2–0.88 mol litre⁻¹ and [CuCl] ≤ 0.012 mol litre⁻¹ and for [NaCl] = 0.2–4.268 mol litre⁻¹ and [CuCl] ≤ 0.047 mol litre⁻¹. The solubility method was used for [NaCl] ≤ 5.0 mol litre⁻¹ and [CuCl] ≤ 1.16 mol litre⁻¹. In the latter case, polynuclear complexes were revealed and the $\beta_{2,4}$ value for Cu₂Cl₄²⁻ was evaluated (Table 1). The constant *pK_s* = 6.73 was also determined by Andrews and Keefer.³²

Table 1. Stability constants ($\bar{\beta}_{m,n}$) for selected $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ complexes.

Temperature / °C	Ionic strength of the solution / mol litre ⁻¹	$\log \bar{\beta}_{1,2}$	$\log \bar{\beta}_{1,3}$	$\log \bar{\beta}_{1,4}$	$\log \bar{\beta}_{2,4}$	pK _s	Ref.
25	0	5.31				6.50	27, 28
20	0	5.30	5.70				29
25	5.0	6.00	5.99	< 4.7	13±0.2	7.38	26
25	6.5 ^a	6.04	5.98	5.6	12.2	6.73	30
25	14.0 ^a	6.30	6.08	5.7	12.8		31

Note: K_s is the solubility product for CuCl_{solid}. ^a The equilibrium constant $\beta_{m,n} = \beta_{m,n}^* / \gamma_{m,n}$; the constant sum of the concentrations ($\tilde{m}$) of $\text{NH}_4\text{Cl} + \text{NH}_4\text{NO}_3$.

With the aim of establishing the compositions of copper(I) chloride complexes in solutions concentrated with respect to CuCl and NH_4Cl , which were used in catalytic reactions of alkynes,^{3,4,8} the equilibria in the $\text{NH}_4\text{Cl} - \text{CuCl} - \text{H}_2\text{O}$ system were examined at 25, 50 and 80 °C at the concentrations of CuCl varying from 0.03 to 10 $\tilde{m}$ (at 80 °C) and at different constant concentrations of the supporting electrolyte, viz., $\text{NH}_4\text{Cl} + \text{NH}_4\text{NO}_3$ (6.5, 10 and 14 $\tilde{m}$).^{30,31,33} The activities of the Cu^+ (a_{Cu^+}) and Cl^- (a_{Cl^-}) ions used in the cited studies were calculated based on the potentials of copper and silver-chloride electrodes measured in chains with transference (with respect to a standard hydrogen electrode). For the standard conditions ($p_{\text{H}_2} = 1$ atm, $a_{\text{H}^+} = 1$, $a_{\text{Cu}^0} = 1$, $a_{\text{AgCl(solid)}} = 1$, $a_{\text{Ag}^0} = 1$), these activities are directly proportional to the thermodynamic activities of individual Cu^+ and Cl^- ions and are taken as equal to these values at $E_D = 0$ (E_D is the diffusion potential). Under the conditions of $E_D = \text{const}$,^{30,31,33} the proportionality coefficient (which is close to unity) remains constant throughout the concentration ranges of CuCl and NH_4Cl , which made it possible to obtain reliable data on the compositions of the complexes. The activity coefficient of Cl^- (γ_{Cl^-}) was found to remain constant at the constant concentration of NH_4^+ ions throughout the concentration ranges of CuCl and NH_4Cl . It was assumed that $\gamma_{(\text{Cu}_m\text{Cl}_n)^{(n-m)-}}$ also remains constant under these conditions. The compositions of polynuclear complexes were determined and the stability constants were estimated using the Sillén–Hedström method.^{34,35} When using the a_{Cu^+} and a_{Cl^-} values, the stability constants $\beta_{m,n}$ differ from the thermodynamic constants $\beta_{m,n}^*$ by the activity coefficient $\gamma_{m,n}$.

$$\beta_{m,n} = \frac{\beta_{m,n}^*}{\gamma_{m,n}}.$$

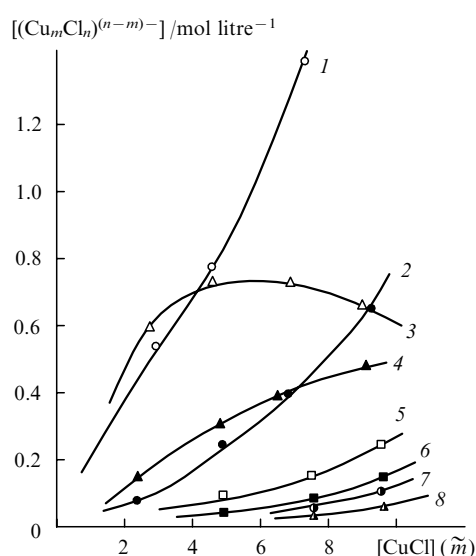
The $\beta_{m,n}$ values for 19 $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ complexes are given in Table 2. It should be taken into account that the $\beta_{m,n}$ constants for complexes with large m (4 or 5) and n (7, 8 or 9) values calculated by this method can exhibit an error of up to one order of magnitude. Hence, it can only be said with assurance that single-, double- and triple-charged anions containing from one to four copper atoms exist in solution. The discrepancy between the experimental and calculated concentrations of CuCl at all temperatures is no higher than 10%.²² It can be seen from Table 2 that the multiply-charged complexes ($n - m = 4$) and complexes with $m = 5$ disappear as the temperature increases, the compositions of the complexes being virtually independent of the increase in $[\text{NH}_4^+]$. The possibility of the determination of a large number of complexes and their compositions by the Sillén–Hedström method follows primarily from the independent determination of the a_{Cu^+} and a_{Cl^-} values. Calculations of the activity (and concentration) of Cl^- ions by the Hedström equation with the use of the a_{Cu^+} , $[\text{CuCl}]_\Sigma$ and $[\text{Cl}^-]_\Sigma$ values demonstrated that the calculated and experimental a_{Cl^-} values coincide only up to the CuCl concentrations of 0.5 $\tilde{m}$. At higher concentrations, the

Table 2. Stability constants ($\beta_{m,n}$) for the reaction $m\text{Cu}^+ + n\text{Cl}^- \rightleftharpoons (\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ at different temperatures and molal concentrations ($\tilde{m}$) of NH_4^+ (see Ref. 31).

Complex anion	25 °C		50 °C	80 °C
	$[\text{NH}_4^+] = 6.5$	$[\text{NH}_4^+] = 14.0$	$[\text{NH}_4^+] = 10.0$	$[\text{NH}_4^+] = 10.0$
CuCl_2^-	1.1×10^6	2.0×10^6	7.0×10^5	4.8×10^5
CuCl_3^{2-}	9.6×10^5	1.2×10^6	2.8×10^5	1.0×10^5
CuCl_4^{3-}	4.0×10^5	5.0×10^5	7.3×10^4	2.0×10^4
Cu_2Cl_3^-	2.0×10^{12}	7.5×10^{12}	1.6×10^{12}	1.3×10^{11}
$\text{Cu}_2\text{Cl}_4^{2-}$	1.5×10^{12}	6.4×10^{12}	7.0×10^{11}	5.0×10^{10}
$\text{Cu}_2\text{Cl}_5^{3-}$	1.0×10^{12}	5.5×10^{12}	4.0×10^{11}	2.8×10^{10}
$\text{Cu}_2\text{Cl}_6^{4-}$	4.3×10^{11}	1.5×10^{12}	2.0×10^{11}	1.0×10^{10}
Cu_3Cl_4^-	3.6×10^{18}	1.7×10^{19}	1.5×10^{18}	3.0×10^{16}
$\text{Cu}_3\text{Cl}_5^{2-}$	4.0×10^{18}	2.3×10^{19}	1.1×10^{18}	3.0×10^{16}
$\text{Cu}_3\text{Cl}_6^{3-}$	2.8×10^{18}	1.7×10^{19}	5.0×10^{17}	7.0×10^{15}
$\text{Cu}_3\text{Cl}_7^{4-}$	1.8×10^{18}	1.5×10^{19}	3.0×10^{17}	—
Cu_4Cl_5^-	2.0×10^{25}	2.4×10^{26}	3.0×10^{24}	6.0×10^{21}
$\text{Cu}_4\text{Cl}_6^{2-}$	2.0×10^{25}	1.2×10^{26}	1.8×10^{24}	5.0×10^{21}
$\text{Cu}_4\text{Cl}_7^{3-}$	5.0×10^{24}	8.0×10^{25}	1.0×10^{24}	—
$\text{Cu}_4\text{Cl}_8^{4-}$	5.0×10^{24}	—	—	—
Cu_5Cl_6^-	1.0×10^{32}	8.0×10^{32}	—	—
$\text{Cu}_5\text{Cl}_7^{2-}$	5.0×10^{31}	8.0×10^{32}	—	—
$\text{Cu}_5\text{Cl}_8^{3-}$	3.0×10^{31}	—	—	—
$\text{Cu}_5\text{Cl}_9^{4-}$	2.0×10^{31}	—	—	—

discrepancy increases due to the low accuracy of the graphical method of solution of the Hedström equation.³⁵

Analysis of the distribution of the complexes (Fig. 3) demonstrated that polynuclear complexes appear in noticeable amounts starting with a CuCl concentration of 3–4 $\tilde{m}$. The total concentration of the $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ complexes with $m = 2, 3$ and 4 reaches ~30% of the sum of the concentrations of all complexes. Based on the $\beta_{m,n}$ values (Table 2) determined at $I = 6.5$ and with the a_{Cu^+} and a_{Cl^-} values, which were measured²⁶ for the maximum concentrations of NaCl and CuCl, it can be demonstrated that the mole fraction of complexes with $m \geq 2$ is smaller than

**Figure 3.** Distribution of the $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ complexes in the $\text{CuCl} - \text{NH}_4\text{Cl} - \text{H}_2\text{O}$ system depending on the concentration of CuCl (80 °C, $[\text{NH}_4^+] = 10 \tilde{m}$).

(1) CuCl_2^- ; (2) Cu_2Cl_3^- ; (3) CuCl_3^{2-} ; (4) $\text{Cu}_2\text{Cl}_4^{2-}$; (5) $\text{Cu}_3\text{Cl}_5^{2-}$; (6) Cu_3Cl_4^- ; (7) $\text{Cu}_4\text{Cl}_6^{2-}$; (8) Cu_4Cl_5^- .

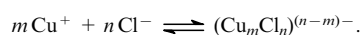
Table 3. Enthalpy of the reaction $m\text{Cu}^+ + n\text{Cl}^- \rightleftharpoons (\text{Cu}_m\text{Cl}_n)^{(n-m)-}$.

$(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$	ΔH_{298}° /kJ mol ⁻¹	$(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$	ΔH_{298}° /kJ mol ⁻¹
CuCl_2^-	-17.1 ± 2	$\text{Cu}_2\text{Cl}_6^{4-}$	-70.6 ± 4
CuCl_3^{2-}	-36.3 ± 2	Cu_3Cl_4^-	-89.5 ± 6
CuCl_4^{3-}	-48.5 ± 2	$\text{Cu}_3\text{Cl}_5^{2-}$	-93.6 ± 6
Cu_2Cl_3^-	-55.6 ± 4	$\text{Cu}_3\text{Cl}_6^{3-}$	-111.5 ± 6
$\text{Cu}_2\text{Cl}_4^{2-}$	-66.9 ± 4	Cu_4Cl_5^-	-139.6 ± 10
$\text{Cu}_2\text{Cl}_5^{3-}$	-73.6 ± 4	$\text{Cu}_4\text{Cl}_6^{2-}$	-147.1 ± 10

Note. $[\text{NH}_4^+] = 10 \text{ } \tilde{m}$.

5%. Because of this, these complexes were not determined experimentally.²⁶ Interestingly, the different approaches gave close values of the stability constants $\beta_{m,n}$ and $\beta_{m,n}$ for CuCl_2^- and CuCl_3^{2-} (see Table 1).

Since the activity coefficients of different chlorides (KCl, NaCl and NH_4Cl) in aqueous solutions are virtually independent of the temperature, it was assumed that $d\gamma_{m,n}/dT \approx 0$. This assumption was used for the estimation of the ΔH values of the reactions³³ (Table 3)



The $\beta_{m,n}$ values change in parallel with the temperature (the dependence of $\log\beta_{m,n}$ on $1/T$ is linear).³³ The $\beta_{m,n}$ values at 25°C and at $[\text{NH}_4^+] = 10 \text{ } \tilde{m}$ were determined by the linear interpolation of the values given in Table 2. The addition of each successive CuCl molecule to the $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ complex causes a decrease in the ΔH value, on the average, by $30\text{--}42 \text{ kJ mol}^{-1}$. According to the estimates obtained, the formation of polynuclear complexes from smaller complexes is also accompanied by a decrease in the enthalpy (Table 4). However, the equilibria are noticeably shifted to the right at rather low temperatures (below $50\text{--}60^\circ\text{C}$) due to a large decrease in the entropy. An increase in the $\beta_{m,n}$ values as the concentration of the cations increases may be associated both with the decrease in $\gamma_{m,n}$ and with the formation of outer-sphere complexes with the NH_4^+ ion. The effect of the anionic complexes with $n-m \geq 2$ on the ionic strength of the solution was assessed¹³ with the use of the Moiseev–Flid equation,^{36,37} which describes the dependence of the acidity function of HCl ($-H_0$) on the ionic strength of the solution (I).

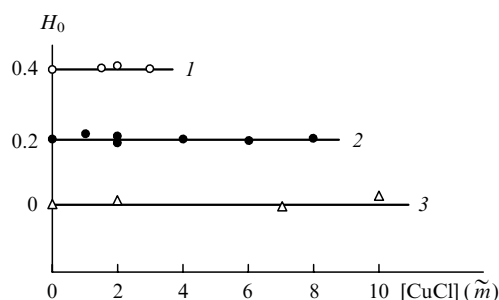
$$-H_0 = \log c_{\text{H}_3\text{O}^+} + LI - \log a_{\text{H}_2\text{O}},$$

where L is a constant dependent on the nature of the salt and the solvent ($L = 0.051 \text{ } \tilde{m}^{-1} \equiv 0.063 \text{ mol}^{-1} \text{ litre}$ at $40\text{--}80^\circ\text{C}$ and $[\text{HCl}] = 0.18\text{--}0.8 \text{ } \tilde{m}$).

The measurements demonstrated³⁸ that the H_0 value remained unchanged over a wide range of CuCl concentrations at $[\text{HCl}] = 0.16 \text{ } \tilde{m}$ (80°C) (Fig. 4).¹³ Taking into account the change in the $a_{\text{H}_2\text{O}}$ value, the ionic strength increases by no more than 0.5 for $[\text{NH}_4\text{Cl}] = 12 \text{ } \tilde{m}$ on going from the $\text{NH}_4\text{Cl}\text{--HCl}\text{--H}_2\text{O}$ system to the $\text{NH}_4\text{Cl}\text{--CuCl}\text{--HCl}\text{--H}_2\text{O}$ system. Hence it follows that multiply-charged anions have virtually no effect on the ionic strength due to their low concentrations (calculated from the data in Table 2) as well as due to

Table 4. Thermodynamic parameters for the association reactions.

Reactions	ΔH_{298}° /kJ mol ⁻¹	ΔS_{298}° /J mol ⁻¹ K ⁻¹
$\text{CuCl}_2^- + \text{CuCl}_2^- \rightleftharpoons \text{Cu}_2\text{Cl}_4^{2-}$	-31.8	-100.3
$\text{CuCl}_2^- + \text{Cu}_2\text{Cl}_3^- \rightleftharpoons \text{Cu}_3\text{Cl}_5^{2-}$	-20.9	-62.7
$\text{CuCl}_2^- + \text{Cu}_3\text{Cl}_4^- \rightleftharpoons \text{Cu}_4\text{Cl}_6^{2-}$	-40.5	-121.2
$\text{Cu}_2\text{Cl}_3^- + \text{Cu}_2\text{Cl}_3^- \rightleftharpoons \text{Cu}_4\text{Cl}_6^{2-}$	-35.9	-112.8

**Figure 4.** Effect of the concentration of CuCl on the acidity function H_0 at 80°C and at different concentrations of NH_4Cl ($[\text{HCl}] = 0.16 \text{ } \tilde{m}$).¹³ $[\text{NH}_4\text{Cl}]$: (1) $5 \text{ } \tilde{m}$; (2) $9 \text{ } \tilde{m}$; (3) $12 \text{ } \tilde{m}$.

their interactions with NH_4^+ ions. Therefore, the $\beta_{m,n}$ value (taking into account the coordination of water) should be represented by the following equation:³¹

$$\beta_{m,n} = \sum_p \sum_q \frac{\beta_{m,n}^*}{\gamma_{m,n,p,q}} a_{\text{NH}_4^+}^p a_{\text{H}_2\text{O}}^q.$$

The presence of various polynuclear complexes and their participation in catalytic reactions were confirmed in subsequent studies of ethynyl complexes of copper in solution, research on the synthesis and isolation of crystalline complexes and investigations on the kinetics of the reactions catalysed by copper(I) complexes.

3. Crystal chemistry of $(\text{Cu}_m\text{X}_n)^{(n-m)-}$ anionic complexes

Analysis of the available information on the compositions and crystal structures of complexes isolated from copper halide systems is necessary for an understanding of the mechanisms of catalytic processes and reasons for high catalytic activities of concentrated solutions containing polynuclear copper complexes. In this section, we analyse the structures of the $(\text{Cu}_m\text{X}_n)^{(n-m)-}$ anions and consider the effect of the outer-sphere M^+ cation on the structures of the complexes.

All types of $(\text{Cu}_m\text{X}_n)^{(n-m)-}$ anions found in the structures of copper(I) halide complexes can be divided into four groups, viz., island, chain (including ribbon), layered and framework structures. The structural classification of the $(\text{Cu}_m\text{X}_n)^{(n-m)-}$ anions is given in Table 5.

Crystal-chemical analysis of the complexes demonstrated that the copper atoms in the $(\text{Cu}_m\text{X}_n)^{(n-m)-}$ anionic fragments ($\text{X} = \text{Cl}$ or Br) are most often located in a tetrahedral environment (the coordination number is 4) formed by the Cl or Br atoms. The vertices of the tetrahedra are generally located at different distances from the central atom. The $\text{X}\text{--Cu}$ bond lengths depend on the coordination number of the X atom, i.e., on the degree of association of the Cu(I) coordination polyhedra. On the whole, the X atoms characterised by larger coordination numbers are located at larger distances from the central atom (see Table 5).

Planar-trigonal coordination (the coordination number is 3) about the Cu atoms was also found in copper(I) halide complexes. The angular or linear environments (the coordination number is 2) occur more rarely. Among the structurally characterised copper(I) halide complexes, no isolated tetrahedral CuX_4^{3-} anions were found. Apparently, discrete CuX_3^{2-} anions containing the metal atom in a planar-trigonal environment also do not exist.

In the $(\text{Cu}_m\text{X}_n)^{(n-m)-}$ anions containing two or more Cu atoms, the coordination polyhedra can be linked to each other in different fashions, viz., through vertices, edges or faces. The coordination polyhedra are more often linked in a combined mode simultaneously through vertices and edges, which in some cases gives rise to $(\text{Cu}_m\text{X}_n)^{(n-m)-}$ anions with zeolite-like structures. The numerous cavities of the latter structures can be occupied by small molecules ($\text{HC}\equiv\text{CH}$, H_2O , $\text{CuC}\equiv\text{CH}$, etc.) and even complexes [for example, the Cu(II) complexes in com-

Table 5. Structural characteristics of the $(\text{Cu}_m\text{X}_n)^{(n-m)-}$ anions in copper(I) halide complexes.

Compound	Anion	Structural type	Coordination number of Cu	Interatomic distances / Å					Ref.
				Cl—Cu ^a	μ_2 -Cl—Cu	μ_3 -Cl—Cu	μ_4 -Cl—Cu	Cu...Cu	
(PyH)CuCl ₂ (1)	CuX ₂ [−]	chain	4, 3	2.269(4), 2.269(4)	2.353(4), 2.433(4)			2.803(5)	39
KCuBr ₂ · 1/2 H ₂ O (2a) ^b	CuX ₂ [−]	layered	4		2.44(1), 2.545(8)			2.891(8)	40
NH ₄ CuBr ₂ · 1/2 H ₂ O (2b) ^b	CuX ₂ [−]	"	4		2.44(1), 2.545(8)			2.891(8)	18
K ₂ CuCl ₃ (3a)	CuX ₃ ^{2−}	chain	4	2.34(2), 2.35(2)	2.44(2), 2.48(2)			4.08(1)	41
K ₂ CuBr ₃ (3b) ^b	CuX ₃ ^{2−}	"	4	2.34(2), 2.35(2)	2.44(2), 2.48(2)			4.08(1)	41
(NH ₄) ₂ CuBr ₃ (3c) ^b	CuX ₃ ^{2−}	"	4	2.34(2), 2.35(2)	2.44(2), 2.48(2)			4.08(1)	42, 43
(NH ₄) ₂ CuCl ₃ (4)	CuX ₃ ^{2−}	"	4	2.34(2), 2.35(2)	2.44(2), 2.48(2)			4.08(1)	43
CsCu ₂ Cl ₃ (5)	Cu ₂ X ₃ [−]	chain (II)	4		2.37(1), 2.37(1)		2.45(1), 2.45(1)	2.81(1)	44
(ImH)Cu ₂ Cl ₃ (6) ^c	Cu ₂ X ₃ [−]	chain (I)	4, 3		2.283(4), 2.366(4)	2.375(3), 2.513(4)		2.748(3)	45
Cs ₃ Cu ₂ Cl ₅ (7)	Cu ₂ X ₅ ^{3−}	chain	4	2.262(5), 2.262(5)			2.34(1), 2.881(8)	2.911(8)	46
(Me ₄ N) ₃ Cu ₂ Br ₅ (8) ^b	Cu ₂ X ₅ ^{3−}	island	3	2.38(1), 2.38(1)	2.40(1), 2.40(1)			—	47
(NH ₄) ₂ Cu ₃ Cl ₅ · 1/3 H ₂ O · 1/15 CuCl (9a)	Cu ₃ X ₅ ^{2−}	framework	4, 3 + 1		2.25(1), 2.30(1)	2.30(1), 2.71(1)	2.40(1), 2.68(1)	2.98(1)	48
(NH ₄) ₂ Cu ₃ Cl ₅ · 4/9 H ₂ O · 1/9 C ₂ H ₂ (9b) ^d	Cu ₃ X ₅ ^{2−}	"	4, 3 + 1		2.25(1), 2.30(1)	2.30(1), 2.71(1)	2.40(1), 2.68(1)	2.98(1)	49
(NH ₄) ₂ Cu ₃ Cl ₅ · 4/9 H ₂ O · 4/9 C ₂ H ₂ (9c) ^d	Cu ₃ X ₅ ^{2−}	"	4, 3 + 1		2.25(1), 2.30(1)	2.30(1), 2.71(1)	2.40(1), 2.68(1)	2.98(1)	49
Rb ₉ Cu ₁₃ Cl ₂₂ · (H ₃ O ⁺ Cl [−]) (9d)	Cu ₃ X ₅ ^{2−}	"	4, 3 + 1		2.25(1), 2.30(1)	2.30(1), 2.71(1)	2.40(1), 2.68(1)	2.98(1)	48
NH ₄ Cu ₄ Cl ₃ (I,Cl) ₂ (10)	Cu ₄ X ₅ [−]	chain	4	2.29(2), 2.39(2)			2.60(2), 2.74(2)	2.48(2)	50
(C ₆ H ₅ NH ₃) ₃ Cu ₄ Cl ₇ (11)	Cu ₄ X ₇ ^{3−}	"	4, 3	2.549(7), 2.549(7)	2.240(8), 2.41(1)	2.56(1), 2.631(8)		2.801(9)	51
(PyH) ₂ Cu ₅ Cl ₇ · 1/5 H ₂ O (12)	Cu ₅ X ₇ ^{2−}	framework	4, 3	2.31(2), 2.31(2)	2.24(2), 2.64(2)	2.48(2), 2.63(2)		2.74(2)	18
Rb ₄ Cu ₅ Cl ₉ (13)	Cu ₅ X ₉ ^{4−}	chain (ribbon)	4		2.196(5), 2.578(5)	2.299(6), 2.652(5)		3.092(4)	52
(MeEt ₃ N) ₅ Cu ₆ Br ₉ (14) ^b	Cu ₆ X ₉ ^{3−}	island	4, 2		2.386(3), 2.528(2)		2.697(3), 2.697(3)	2.650(3)	53
Rb ₁₁ Cu ₁₅ Cl ₁₆ Br ₆ (Cu ^{II} Cl ₆) · CuC≡CH (15a)	Cu ₁₅ X ₂₄ ^{9−}	layered	4, 2		2.287(7), 2.340(7)	2.305(7), 2.63(1)		3.006(6)	54
Rb ₁₁ Cu ₁₅ Cl ₁₆ Br ₆ (Cu ^{II} Cl ₆) (15b)	Cu ₁₅ X ₂₄ ^{9−}	"	4, 2		2.287(7), 2.340(7)	2.305(7), 2.63(1)		3.006(6)	54
{Rb ₁₁ [Cu ₂ (H ₂ O) ₂]}Cu ₁₅ Cl ₂₄ (Cu ^{II} Cl ₆) (16)	Cu ₁₅ X ₂₄ ^{9−}	"	4, 2		2.287(7), 2.340(7)	2.305(7), 2.63(1)		3.006(6)	55

Notes. For the Cu—Cl bonds, the first and second figures correspond to the minimum and maximum values, respectively; for the Cu—Cu bonds, the shortest distances are given. The complexes **2a** and **2b**, the complexes **3a**–**c** and **4**, the complexes **9a**–**d** and the complexes **15a,b** and **16** are isostructural. ^a The distances from the Cu atom to the nonbridging Cl atom; ^b the Cu—Br bond lengths are given; ^c ImH is the imidazolium cation; ^d acetylene is adsorbed and does not occupy particular crystallographic positions.

pounds **15a,b** and **16**; see Table 5] to form 'guest–host' systems. The fact that the coordination polyhedra about the Cu atoms are linked *via* edges (faces) results in short Cu...Cu contacts typical of cluster compounds (see Table 5).

Let us consider the types of the $(\text{Cu}_m\text{X}_n)^{(n-m)-}$ anions found in the structures of copper(I) halide complexes in detail. Two types of mononuclear anions, *viz.*, CuX_2^- and CuX_3^{2-} , are known. The CuX_2^- anion serves as an independent unit of the $(\text{CuX}_2)_n$ polymeric anions, which exist as chains or layers in complexes **1** and **2a,b**, respectively (see Table 5). In both case, the coordination polyhedra about the Cu atoms are linked to each other both through vertices and edges.

In isostructural compounds **3a** (or **3b,c**) and **4**, the $(\text{CuX}_3^{2-})_n$ chain fragments of identical structure are formed based on the CuX_3^{2-} anion. In these compounds, the coordination tetrahedra about the Cu(I) atoms are linked only through vertices.

The binuclear Cu_2X_3^- anion can produce two types of $(\text{Cu}_2\text{Cl}_3)_n$ chain fragments. Fragments of the first type are observed in complex **6** and are formed by the Cu(I) coordination tetrahedra and triangles linked to each other simultaneously through vertices and edges. The second type (complex **5**) is formed by the Cu(I) coordination tetrahedra linked to each other exclusively through edges.

For yet another binuclear $\text{Cu}_2\text{X}_5^{3-}$ anion, both the island and chain modes of arrangement of the anionic fragments are observed. Complex **8** contains the $\text{Cu}_2\text{Br}_5^{3-}$ anion of the island type. In this complex, two coordination triangles about the Cu(I) atoms are linked *via* a shared vertex. In complex **7**, the $(\text{Cu}_2\text{Cl}_5^{3-})_n$ chain anion consists only of the Cu(I) coordination tetrahedra, which are linked to each other both through vertices and edges.

The trinuclear $\text{Cu}_3\text{X}_5^{3-}$ anion was found in isotopic compounds **9a–c** with the zeolite-like framework structures formed by the Cu(I) coordination polyhedra linked to each other both through vertices and edges. The $(\text{Cu}_3\text{Cl}_5^{3-})_n$ framework anion was also found in complex **9d** whose composition can be represented as $\text{Rb}_2\text{Cu}_{3-x}\text{Cl}_{5-x} \cdot (2/9\text{H}_3\text{O}^+ + \text{Cl}^-)$ ($x = 0.1$) by analogy with the compounds **9a–c**. Crystals of these four compounds were isolated from the catalytic $\text{MCl–CuCl–H}_2\text{O}$ system ($\text{M} = \text{NH}_4^+$ or Rb^+) in the presence of which oligomerisation of C_2H_2 was performed. The compounds **9a–d** can be considered as stable stoichiometric points in the region of a phase with the variable composition $\text{M}_2\text{Cu}_3\text{Cl}_5 \cdot x \cdot (y\text{C}_2\text{H}_2)$, where $x = 3/9\text{H}_2\text{O} \cdot 1/15\text{CuCl}$ and $(2/9\text{H}_3\text{O}^+ + \text{Cl}^-)$ at $y = 0$ for $\text{M} = \text{NH}_4^+$ and Rb^+ , respectively, and $x = 4/9\text{H}_2\text{O}$ at $y = 1/9$ or $4/9$ for $\text{M} = \text{NH}_4^+$.

The tetranuclear Cu_4X_5^- anion forms an unusual [from the viewpoint of the mode in which the coordination polyhedra about the Cu(I) atoms are linked] $(\text{Cu}_4\text{X}_5)_n$ chain fragment. In complex **10**, these fragments exist as the Cu(I) coordination tetrahedra linked to each other *via* edges and faces.

The tetranuclear $\text{Cu}_4\text{X}_7^{2-}$ anion is observed in complex **11**. These anions form $(\text{Cu}_4\text{Cl}_7^{2-})_n$ chains in which the coordination tetrahedra and triangles about Cu(I) are linked to each other through vertices and edges.

In the structurally characterised copper(I) halide complexes, two types of pentanuclear anions, *viz.*, $\text{Cu}_5\text{X}_7^{2-}$ and $\text{Cu}_5\text{X}_9^{4-}$, were found. In complex **12**, the $(\text{Cu}_5\text{Cl}_7^{2-})_n$ anions are built of the coordination tetrahedra and triangles about the Cu(I) atoms, which are successively linked to each other through vertices and edges to form a zeolite-like framework structure.

The $\text{Cu}_5\text{X}_9^{4-}$ anions in complex **13** are linked in a ribbon-like $(\text{Cu}_5\text{X}_9^{4-})_n$ fragment in which the Cu(I) coordination polyhedra are linked to each other both through vertices and edges.

The island $\text{Cu}_6\text{Br}_9^{3-}$ fragment is an example of a hexanuclear anion. In complex **14**, this anion consists of four Cu(I) coordination tetrahedra linked to each other exclusively through edges. Two opposite vertices of this fragment are additionally coordinated by two Cu atoms with the coordination number 2.

Finally, the polynuclear $\text{Cu}_{15}\text{X}_{24}^{9-}$ anion was found in the zeolite-like structure **16**. The anions form a $[\text{Cu}_{15}\text{Cl}_{24}(\text{Cu}^{\text{II}}\text{Cl}_6)]_n$ layer in which the coordination polyhedra about Cu(I) are linked

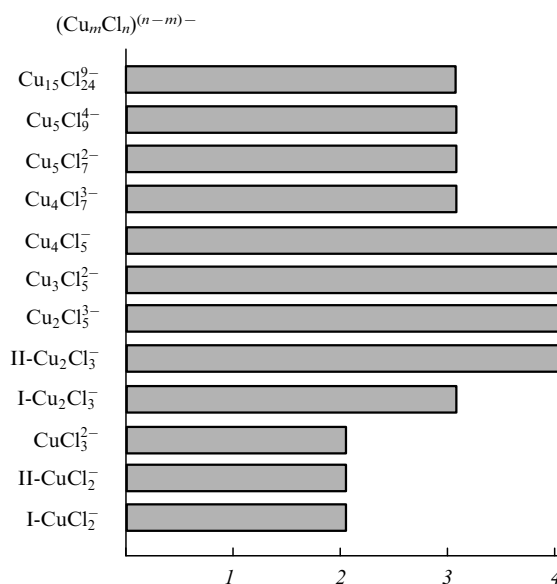


Figure 5. Relationship between the degree of association of the coordination polyhedra about the metal atoms and the number of nuclei (m) for the $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ anion; (1) terminal Cl; (2), (3) and (4) μ_2 -, μ_3 - and μ_4 -Cl, respectively.

to each other through vertices and edges. The 'guest–host'-type structures of **15a,b** contain the structurally similar $[\text{Cu}_{15}\text{Cl}_{16}\text{Br}_6(\text{Cu}^{\text{II}}\text{Cl}_6)]_n$ anionic layers in which some crystallographic positions are partially occupied by Cl atoms.

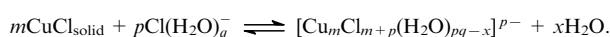
For a range of the above-described structural fragments in copper(I) chloride complexes, a marked trend is observed toward their complication as the number of nuclei in the $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ anions increases. The relationship between the number of nuclei in the $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ fragment (m) and the character of the bridging Cl atom (μ_n , where $n = 2, 3$ or 4) can be represented by a diagram (Fig. 5). It can be readily seen from Fig. 5 that an increase in m is accompanied by an increase in the ability of the chlorine atoms to act as bridging ligands. Thus, the very low degree of association of the Cu(I) coordination polyhedra is characteristic of the anionic fragments at $m = 1$, whereas complex structural forms of anions appear at $m = 2, 3$ or 4 . For $m \geq 4$, though the ability of the bridging chlorine atoms to undergo association is somewhat lower, the structural fragments are, on the whole, complex.

This regularity agrees well with the results of studies of the equilibria in the CuCl–MCl system.^{13, 30, 31, 33} Thus among the $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ complexes ($m = 1–5$ and $n = 2–7$), which are present in concentrated solutions of NH_4Cl and CuCl , the complexes with $m = 2, 3$ and 4 prevail. Therefore, the ability of the Cu(I) coordination polyhedra to form complex $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ associates at $m \geq 2, 3$ or 4 is, apparently, one of the major reasons for the high catalytic activity of concentrated solutions of MCl and CuCl .

Complex associates in solution are formed from coordination polyhedra of layered, chain, island or framework types upon cleavage of the bridging $\mu_n\text{-Cl}$ bonds by water molecules or Cl^- anions, which occupy the coordination vacancies in $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ complexes in solutions.

Let us consider the effect of the nature of the outer-sphere M^+ cation involved in the $\text{MCl–CuCl–H}_2\text{O}$ system on the crystal structures of the anionic copper(I) halide complexes.

As mentioned above, dissolution of CuCl and formation of anionic complexes in aqueous solutions of MCl proceed according to the reaction



It is known that copper chloride is a salt, which contains covalent polar Cu–Cl bonds and is characterised by a framework sphalerite-like structure.⁵⁶ Dissolution of CuCl in aqueous solutions of ionic salts MCl involves destruction of the crystal lattice of CuCl under the action of adsorbed Cl[−] anions with the simultaneous cleavage of some Cu–Cl bonds and the appearance of individual (Cu_mCl_n)^{(n−m)−} fragments resulting in the establishment of the equilibria between these fragments. Both processes are accompanied by dehydration of Cl[−] ions present in the solution. Apparently, the structures of the anions (as well as the stoichiometry of the equilibria) are determined to a large extent by the nature of the M⁺ cations. The crystal structures of the complexes isolated from solutions also depend on the type (the size, symmetry, configuration, charge density and other characteristics) of the outer-sphere cation involved in complexation.

Analysis of the structural data demonstrated that NH₄⁺ cations can form crystalline complexes with extremely complex zeolite-like structures, such as the complexes **9a–c**, due to the tetrahedral form of the ammonium cations. The latter interact with Cl[−] ions through N(H)⋯Cl hydrogen bonds⁵⁷ imparting the directed character to the M⁺⋯Cl[−] ionic bonding, which is responsible for the ‘code’ of the structure construction of the complex as a whole. The skeleton structures **1**, **6**, **11** and **12** containing planar PyH⁺, ImH⁺ (Im is imidazole) and C₆H₅NH₃⁺ cations are also formed through (N)H⋯Cl hydrogen bonds. The replacement of NH₄Cl by KCl gives rise to the complexes **2a**, **3a** and **3b** in which K⁺ cations cannot form directed bonds with Cl[−] ions, and, consequently, no complex combinations of the Cu(I) coordination polyhedra are observed.

Apparently, the ability of NH₄⁺ cations and protonated amines to generate complex structural forms of (Cu_mCl_n)^{(n−m)−} anions through spatially oriented M⁺⋯Cl[−] interactions giving rise to outer-sphere complexes in solution is one of the reasons for the fact that catalytic activities in systems containing NH₄⁺ and amine hydrochlorides are higher than those in the KCl–CuCl–H₂O systems.

III. Organocopper compounds

In the previous section, we considered M_(n−m)Cu_mX_n complexes, which were formed in concentrated aqueous solutions of MCl and CuCl and isolated from solutions in the crystalline state. The compositions and structures of these complexes give an idea of the state of the initial catalytic system. In the course of the reaction of the MCl–CuCl–H₂O system with acetylene (for example, under conditions of the oligomerisation according to Nieuwland), acetylene molecules and then products of their conversions (mono- and disubstituted derivatives) form π- and σ-organocopper compounds with (Cu_mCl_n)^{(n−m)−} anions.^{4,13}

In the first stage, π-complexes form. Then these complexes are converted into compounds of the mono- and diacetylenide types depending on pH of the medium.⁵⁸ In the initially weakly acidic medium, organometallic compounds exist predominantly as acetylenide (ethynyl) derivatives, which can be reversibly converted into π-complexes as pH decreases. The latter complexes are the major products of the reactions of alkynes with Cu(I) in acidic solutions. In this section, we will consider π- and σ-organocopper complexes, which are formed in the course of the reactions of acetylenic compounds with concentrated aqueous solutions of MCl and CuCl. Analysis of the structural features of polynuclear ethynyl complexes of copper(I) is required for an understanding of their role in catalytic processes (provided that the structures of the major fragments of the crystalline compounds are retained in solution). Selected structural characteristics of the compounds under consideration are given in Tables 6–9. For simplicity, the types (modes) of coordination of the C≡C group (η¹ or η²) are denoted by σ or π, respectively (or σ,π-mode if both modes of coordination occur).

Examination of the data given in Tables 6–9 allows one to judge the efficiency of π-interactions in copper(I) π-complexes, to estimate the degree of activation of the triple bond and the alkyne molecule by the metal ion, to follow the possible pathways of conversions of π-complexes into acetylenide (ethynyl) complexes

Table 6. Mode of coordination of the C≡C group and the geometric characteristics of the π-coordinated Cu(I) units in the structures of π-complexes of copper(I) halides with acetylene and its monosubstituted derivatives.

Complex	Mode of coordination of the C≡C group	Cu–C* distance /Å	Sum of LCuL angles in the base of the polyhedron /deg	Cu–X _{ax} bond length /Å	Difference in Cu–C distances /Å	C≡C bond length /Å	Ref.
Cu ₂ Cl ₂ (HC≡CH) (17)	μ-η ² ,η ²	2.01(8)	356.1	2.75(3)	0.00(8)	1.18(14)	20
		1.76(8)	359.4	3.08(4)	0.00(8)		
		2.12(7)	356.5	3.07(4)	0.11(7)	1.26(13)	
		1.99(9)	350.5	2.67(3)	0.07(9)		
		2.16(9)	348.9	2.99(5)	0.00(9)	0.94(24) ^a	
		2.29(9)	351.5	2.74(4)	0.00(9)		
Cu ₃ Cl ₃ (HC≡CH) (18)	μ-η ² ,η ²	2.01(3)	352.8	2.663(6)	0.08(3)	1.12(4) ^a	20
		2.01(3)	352.8	2.663(6)	0.08(3)		
		1.97(2)	349.4	2.596(7)	0.02(2)	1.32(5)	
		1.97(2)	349.4	2.596(7)	0.02(2)		
Cu ₆ Cl ₆ (HC≡CH) (19) ^b	μ-η ² ,η ²	—	—	—	—	—	17
KCu ₃ Cl ₄ (HC≡CH) (20)	μ-η ² ,η ²	1.940(4)	359.2	3.177(2)	0.011(4)	1.26(1)	20
		1.940(4)	359.2	3.177(2)	0.011(4)		
		1.947(4)	359.5	3.462(2)	0.004(4)	1.28(1)	
		1.947(4)	359.5	3.462(2)	0.004(4)		
NH ₄ Cu ₃ Cl ₄ (HC≡CH) (21a)	μ-η ² ,η ²	1.94(1)	359.3	3.664(5)	0.00(1)	1.32(2)	59
		1.94(1)	359.4	3.583(5)	0.00(1)		
		1.93(1)	359.0	3.256(5)	0.03(1)	1.25(1)	
		1.93(1)	359.0	3.256(5)	0.03(1)		
RbCu ₃ Cl ₄ (HC≡CH) (21b)	μ-η ² ,η ²	2.03(3)	359.5	3.674(9)	0.00(3)	1.33(3)	60
		1.93(3)	359.9	3.596(9)	0.00(3)		
		1.89(2)	358.5	3.307(9)	0.04(2)	1.27(3)	
		1.89(2)	358.5	3.307(9)	0.04(2)		

Table 6 (continued).

Complex	Mode of coordination of the C≡C group	Cu—C* distance /Å	Sum of LCuL angles in the base of the polyhedron /deg	Cu—X _{ax} bond length /Å	Difference in Cu—C distances /Å	C≡C bond length /Å	Ref.
KCu ₈ Cl ₉ (HC≡CH) ₄ ·1/2 HCu ₂ Cl ₃ ·H ₂ O (22)	μ-η ² ,η ²	1.948(4)	356.7	2.832(2)	0.000(4)	1.23(1)	20
		1.948(4)	356.7	2.832(2)	0.000(4)		
NH ₄ Cu ₈ Cl ₉ (HC≡CH) ₄ ·2/5 {[Cu(H ₂ O) ₂]·[CuCl ₂]·H ₂ O} (23)	μ-η ² ,η ²	1.957(5)	356.9	2.846(4)	0.000(5)	1.233(9)	61
		1.957(5)	356.9	2.846(4)	0.000(5)		
CuCl(HC≡CPh) (24)	η ²	1.941(4)	358.8	3.037(1)	0.067(4)	1.213(5)	62
CuCl(HC≡CCH ₂ Cl) (25)	η ²	1.912(4)	358.6	3.102(1)	0.000(4)	1.204(5)	62
CuCl(HC≡CCH ₂ OH) (26)	η ²	1.92(1)	358.7	3.078(4)	0.012(9)	1.20(1)	62
Cu ₂ Cl ₂ (HC≡C(CH ₂) ₄ C≡CH) (27)	η ² ;η ²	1.946(6)	359.7	3.134(2)	0.024(6)	1.196(9)	63
Cu ₂ Cl ₂ (HC≡CCH ₂ OH) (28)	μ-η ² ,η ²	1.94(1)	357.5	2.467(9) ^c	0.00(1)	1.26(2)	64
		1.98(1)	354.7	2.725(5)	0.02(1)		
		1.95(1)	358.7	3.303(6)	0.03(1)	1.24(2)	
		1.99(1)	349.1	2.604(5)	0.04(1)		
		1.91(1)	359.8	3.730(6)	0.01(1)	1.25(2)	
		2.10(1)	341.3	2.416(6)	0.08(1)		
(C ₆ H ₅ NH ₃)Cu ₂ Cl ₃ (HC≡CCH ₂ OH) (29)	μ-η ² ,η ²	1.93(1)	359.8	3.058(7)	0.006(9)	1.27(1)	65
		1.964(9)	354.8	2.830(7)	0.027(9)		

Note. Hereinafter, Cu—C* is the distance from the copper atom to the midpoint of the multiple bond. ^a The positions of the C atoms in the acetylene fragment were not refined because of the low stability of the complexes; ^b the first stage of X-ray diffraction analysis; ^c X_{ax} is the O atom of the alcoholic group.

Table 7. Mode of coordination of the C≡C group and the geometric characteristics of the π-coordinated Cu(I) units in the structures of π-complexes of copper(I) halides with alkynes.

Complex	Mode of coordination of the C≡C group	Cu—C* distance /Å	Sum of LCuL angles in the base of the polyhedron /deg	Cu—X _{ax} bond length /Å	Difference in Cu—C distances /Å	C≡C bond length /Å	Ref.
Cu ₇ Cl ₇ (HC≡CCH=CH ₂) ₃ (30)	μ-η ² ,η ²	1.98(1)	354.2	2.643(6)	0.03(1)	1.26(2)	66
		1.96(2)	353.8	2.647(6)	0.02(2)		
CuCl(CH ₂ =CHCH ₂ C≡CCH ₂ OH) (31)	η ²	1.92(2)	359.5	3.516(7)	0.10(2)	1.14(3) ^a	67
Cu ₂ Cl ₂ (CH ₂ =CHCH ₂ C≡CPh) (32)	η ²	1.953(7) ^b	357.1	2.930(2)	0.063(7)	1.35(1)	68
		1.937(7)	359.1	2.924(2)	0.010(7)	1.23(1)	
Cu ₂ Br ₂ (CH ₂ =CHCH ₂ C≡CPh) (33)	η ²	1.85(12) ^b	357.5	2.63(3)	0.03(12)	1.3(1)	69
		1.94(9)	358.4	3.04(3)	0.03(9)	1.2(1)	
Cu ₂ Cl ₂ (CH ₂ =CHC≡CCH=CH ₂) (34)	η ²	1.961(4) ^b	355.5	2.705(1)	0.050(4)	1.361(6)	70
Cu ₃ Cl ₃ (CH ₂ =CHC≡CCH=CH ₂) (35)	η ²	1.951(7) ^b	359.8	3.147(2)	0.034(6)	1.34(1)	70
		1.962(7) ^b	357.2	2.881(2)	0.008(6)	1.36(1)	
		1.910(6)	359.9	3.380(2)	0.002(5)	1.225(8)	
Cu ₃ Cl ₃ (CH ₂ =CHCH ₂ C≡CCH ₂ CH=CH ₂) (36)	η ²	1.97(1) ^b	350.5	2.627(3)	0.07(1)	1.35(2)	71
		1.86(1)	360.0	3.742(3)	0.00(1)	1.18(2)	
Cu ₃ Br ₃ (CH ₂ =CHCH ₂ C≡CCH ₂ CH=CH ₂) (37a)	η ²	2.00(4) ^b	358.2	3.028(7)	0.12(4)	1.45(5)	71
(modification A)		1.99(4) ^b	353.1	2.895(6)	0.24(3)	1.36(5)	
		2.05(4)	359.5	3.450(6)	0.07(3)	1.21(5)	
Cu ₃ Br ₃ (CH ₂ =CHCH ₂ C≡CCH ₂ CH=CH ₂) (37b)	η ²	1.99(3) ^b	359.6	3.36(3)	0.00(3)	1.37(4)	72
(modification B)		1.98(3) ^b	358.6	3.05(2)	0.10(3)	1.36(4)	
		1.92(3)	359.9	3.33(3)	0.03(2)	1.18(3)	

^a The positions of the corresponding C atoms were not refined because of the disorder of the C≡C groups in the crystal; ^b the Cu(I) atom is coordinated by the C≡C bond.

and to analyse the characteristic structural features of polynuclear ethynyl compounds.

1. Complexes of CuX with acetylene and its derivatives

The triple bond consists (in addition to the σ-bond) of two mutually orthogonal π-bonds, which are potentially able to interact with Cu(I). In the structures of copper(I) chloride complexes, acetylene always acts as a bridging π-ligand and is

coordinated simultaneously by two metal atoms (Fig. 6). In this respect, the acetylene ligand is isolobal to the bridging μ²-Cl ligand. Some monosubstituted acetylene derivatives in π-complexes with CuCl behave analogously (for example, **28–30**; see Tables 6 and 7). However, the C≡C bond in π-complexes of a series of alkynes and alkenynes, for example, of disubstituted acetylene derivatives (like the alkene bond), is coordinated exclusively by one copper atom [compounds **24–27**, **38–42** and **31–37**

Table 8. Mode of coordination of the C≡C group and the geometric characteristics of the π-coordinated Cu(I) units in the structures of π-complexes of copper(I) halides with disubstituted acetylenes.

Complex	Mode of coordination of the C≡C group	Cu—C* distance /Å	Sum of LCuL angles in the base of the polyhedron /deg	Cu—X _{ax} bond length /Å	Difference in Cu—C distances /Å	C≡C bond length /Å	Ref.
CuCl(Me ₃ SiC≡CSiMe ₃) (38)	η ²	1.923(3)	360.0	—	0.003(3)	1.227(5)	73
CuCl(HOCH ₂ C≡CCH ₂ OH) (39a)	η ²	1.928(3)	359.3	3.183(1)	0.024(3)	1.219(4)	40
CuBr(HOCH ₂ C≡CCH ₂ OH) (39b) ^a	η ²	—	—	—	—	—	40
KCuBr ₂ (HOCH ₂ C≡CCH ₂ OH) (40a)	η ²	1.923(7)	359.9	—	0.000(7)	1.24(1)	40
KCuCl ₂ (HOCH ₂ C≡CCH ₂ OH) (40b) ^a	η ²	—	—	—	—	—	40
Cu ₂ Cl ₂ (Bu ^t C≡CSC≡CBu ^t) (41)	η ² ; η ²	1.886(4)	360.0	3.550(3)	0.029(4)	1.232(4)	74
[Cu ₂ Cl ₂ (Bu ^t C≡CSC≡CBu ^t)] _n (42)	η ² ; η ²	1.916(4)	359.8	3.501(3)	0.36(4)	1.071(5) ^b	74
		1.88(2)	359.4	—	0.04(2)	1.25(2)	
		1.87(2)	358.8	3.01(1)	0.12(2)	1.13(2) ^b	
		1.91(2)	359.3	3.34(1)	0.02(2)	1.24(2)	
		1.88(2)	359.3	—	0.09(2)	1.23(2)	

^a The first stage of X-ray diffraction analysis. ^b The positions of the corresponding C atoms were not refined because of the disorder of the C≡C groups in the crystal.

Table 9. Mode of coordination of the C≡C group and the geometric characteristics of the π-coordinated Cu(I) units in the structures of σ,π-complexes of copper(I) halides.

Complex	Mode of coordination of the C≡C group	Cu—C* distance /Å	Sum of LCuL angles in the base of the polyhedron /deg	Cu—X _{ax} bond length /Å	Difference in Cu—C distances /Å	C≡C bond length /Å	Ref.
(ImH) ₄ Cu ₉ Cl ₁₁ (C≡CH) ₂ (43)	μ-η ¹ , η ¹	—	—	—	—	1.21(2)	45
(PyH) ₄ Cu ₉ Cl ₁₂ (C≡CH) (44)	μ-η ¹ , η ¹	—	—	—	—	1.19(7)	39
(NH ₄) ₈ Cu ₂₉ Cl ₂₉ (C≡C) ₄ ·7 H ₂ O (45)	μ ₃ -η ¹ , η ¹ , η ¹ , μ-η ² , η ²	2.18(3)	159.1 ^a	—	0.34(3)	—	75
	μ ₃ -η ¹ , η ¹ , η ¹	2.01(2)	358.4	2.980(9)	0.01(2)	1.27(5) ^b	
	μ ₃ -η ¹ , η ¹ , η ¹	2.01(2)	358.4	2.980(9)	0.01(2)	—	
	μ-η ¹ , η ¹	2.06(2)	359.1	2.79(1)	0.06(2)	1.23(5)	
	μ ₃ -η ² , η ² , η ²	2.06(2)	359.1	2.79(1)	0.06(2)	—	
	μ ₃ -η ¹ , η ¹ , η ¹	—	—	—	—	—	
(ImH)Cu ₄ Cl ₄ (C≡CCH ₂ OH)·H ₂ O (46)	μ-η ¹ , η ¹ , μ-η ² , η ²	2.01(1)	353.9	2.773(5)	0.01(1)	1.29(2)	45
NH ₄ Cu ₄ Cl ₄ (C≡CCH ₂ OH)·H ₂ O (47) ^c	μ-η ¹ , η ¹ , μ-η ² , η ²	—	—	—	—	—	18
	μ-η ¹ , η ¹ , μ-η ² , η ²	1.986(8)	355.9	2.850(3)	0.028(8)	1.29(1)	
(NH ₄) ₂ Cu ₄ Cl ₅ (C≡CCH ₂ OH)·H ₂ O (48)	μ-η ¹ , η ¹ , μ-η ² , η ²	2.005(8)	358.0	2.979(3)	0.028(8)	—	76
		2.01(2)	357.5	2.937(9)	0.04(2)	1.25(4)	
(C ₆ H ₅ NH ₃) ₂ Cu ₄ Cl ₅ (C≡CCH ₂ OH) (49)	μ-η ¹ , η ¹ , μ-η ² , η ²	1.94(3)	359.1	3.061(7)	0.08(2)	1.22(3)	78
		1.98(2)	358.8	3.23(1)	0.03(2)	—	
Rb ₃ Cu ₇ Cl ₉ (C≡CCH ₂ OH)·H ₂ O (51)	μ ₃ -η ¹ , η ¹ , η ¹ , μ-η ² , η ²	2.09(2)	358.9	3.558(7)	0.00(2)	1.23(3)	52
		1.97(2)	359.9	3.489(6)	0.02(2)	—	
(PyH) ₂ Cu ₈ Cl ₈ (C≡CCH ₂ OH) ₂ ·H ₂ O (52)	μ ₃ -η ¹ , η ¹ , η ¹ , μ-η ² , η ²	1.974(5)	356.6	2.973(3)	0.024(5)	1.258(6)	39
		1.994(5)	355.9	2.754(3)	0.009(5)	—	
		1.989(5)	352.8	2.728(3)	0.127(5)	1.267(6)	
		2.020(5)	358.8	2.931(3)	0.009(5)	—	
(C ₆ H ₅ NH ₃) ₃ Cu ₈ Cl ₁₀ (C≡CCH ₂ OH)·2 H ₂ O (53)	μ-η ¹ , η ¹ , μ-η ² , η ²	1.97(1)	360.0	3.392(9)	0.04(1)	1.25(2)	51
		1.98(1)	355.8	2.858(9)	0.02(1)	—	
HO(CH ₂) ₂ NH ₃ Cu ₉ Cl ₈ (C≡CCH ₂ OH) ₂ ·(H ₂ O) ₂ (54)	μ ₃ -η ¹ , η ¹ , η ¹ , μ-η ² , η ²	1.988(6)	356.1	2.778(3)	0.012(7)	1.259(8)	79
		1.965(6)	358.7	2.979(3)	0.069(6)	—	
Cu ₂₅ Cl ₁₇ (C≡CCH=CH ₂) ₈ ·14 H ₂ O (55)	μ-η ¹ , η ¹ , μ-η ² , η ²	1.93(4)	357.7	—	0.03(3)	1.21(5)	66
		2.00(3)	357.2	—	0.03(3)	—	

^a The coordination number of Cu is 2; ^b the η²-mode of coordination of the C≡C group to three Cu(I) atoms; ^c the first stage of X-ray diffraction analysis.

(Fig. 7)]. Moreover, the C≡C bond of the alkenyne ligand (*i.e.*, the more sterically hindered bond) successfully competes with the peripheral vinyl groups even in conjugated systems (complex **35**). In the case of the CuCl complex with allylpropargyl alcohol (**31**), the C=C bond of the allyl group, unlike the C≡C bond, is not coordinated to the copper atom. Therefore, the ability of the

C≡C bond to be involved in the π-interaction with copper(I) is higher than that of the C=C bond.

According to the Dewar–Chatt–Duncanson concept,^{13, 80, 81} the formation of acetylene complexes with Cu(I) compounds (3d¹⁰4s⁰4p⁰) is accompanied by interactions between the frontier molecular orbitals (MO) of acetylene and the metal complex [for

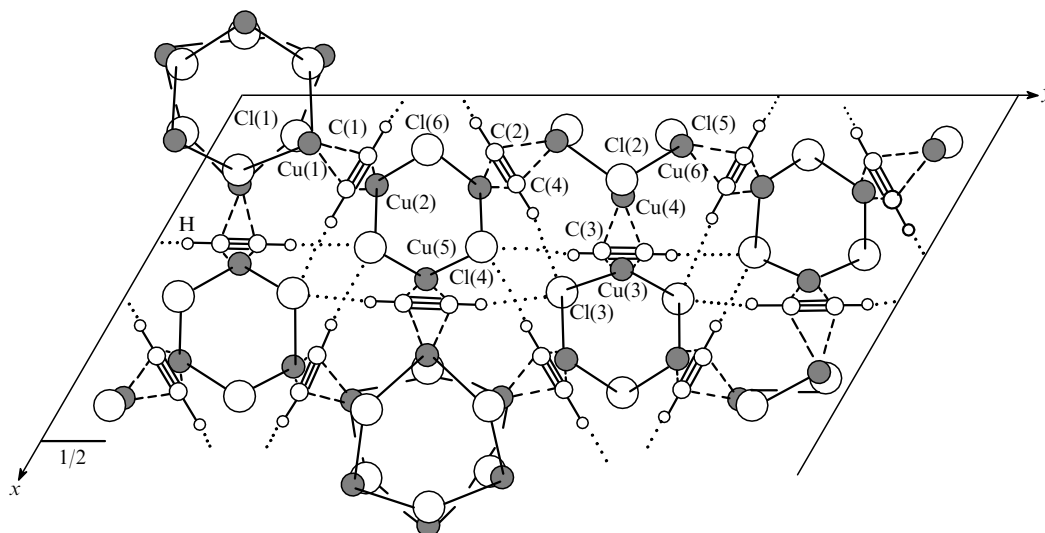


Figure 6. Projection of the structure of $\text{Cu}_2\text{Cl}_2(\text{HC}\equiv\text{CH})$ (**17**) onto the xy plane.

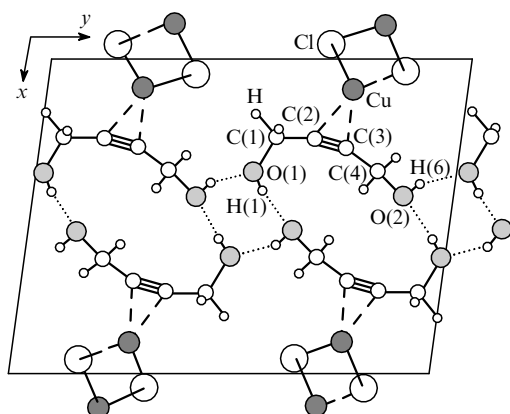


Figure 7. Projection of the structure of $\text{CuC}_2(\text{HOCH}_2\text{C}\equiv\text{CH}_2\text{OH})$ (**39a**) onto the xy plane.

example, $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ giving rise to two three-centre MOs. One of them is formed by the overlap of the unoccupied sp^3 -hybridised orbital of Cu(I) with the bonding π -MO of acetylene (the donor-acceptor component of the $\text{M} \leftarrow \text{L}$ bond, where M is metal and L is alkyne), whereas the second MO is formed due to overlapping of one of the symmetry-suitable occupied d orbitals of the metal atom and the antibonding π^* -MO of acetylene (the dative component of the $\text{M} \rightarrow \text{L}$ bond). Both three-centre bonds contribute to the increase in the strength of the $\text{Cu}-\pi$ -ligand bond; however, they have different effects on the properties of the π -ligand. For example, the occupation of the antibonding π^* -MO of acetylene with the electrons of the metal atom (the dative component) in Cu(I) π -complexes leads to a change in the $\text{C}\equiv\text{C}-\text{R}$ angle (*cis* distortion) and elongation of the $\text{C}\equiv\text{C}$ bond. In turn, donation of electrons from π -MO of acetylene to one of the sp^3 -hybridised orbitals of Cu(I) (the donor-acceptor component) results in a decrease in the electron density on the $\text{C}\equiv\text{C}$ bond due to which the carbon atoms acquire positive charges (δ^+) and this π -coordinated acetylene group acts as a soft electrophile. The transfer of the electron density from the ligand to Cu(I) leads also to a decrease in the distance from the Cu(I) atom to the midpoint of the $\text{C}\equiv\text{C}$ bond.

In essence, the above-considered model of the bond in the metal (M) π -complex with alkyne is synergistic because an increase in the $\text{M} \leftarrow \text{L}$ component leads to an increase in the back $\text{M} \rightarrow \text{L}$ transfer.⁸² However, these components make differ-

ent contributions to π -interactions. Calculations of the energies of the Cu(I)–acetylene bond [or the Cu(I)–ethylene bond] demonstrated⁸³ that the contribution of the donor-acceptor electron transfer to the bond energy is approximately three times larger than that of the dative interaction. Hence, the specificity of activation of the acetylene bond on the metal centre in Cu(I)– π -complexes is primarily determined by interactions of the $\text{M} \leftarrow \text{L}$ type. High-level quantum-chemical calculations^{84,85} of the $\text{Cu}(\text{C}_2\text{H}_2)^+$ complex (taking into account the low-lying excited states) demonstrated that the $\text{Cu}^+ - \text{C}_2\text{H}_2$ bond is predominantly ionic in character and the Coulomb Cu(I) ion– π -ligand interaction makes the major contribution (the $\text{C}\equiv\text{C}$ bond length is 1.242 Å, the $\text{C}\equiv\text{CH}$ angle is 168.7°). This is consistent with the conclusion⁸³ that the electron transfer to the metal atom prevails. The ionic character of the bonds was also revealed in bisalkyne complexes $\text{Cl}_2\text{X}(\text{C}\equiv\text{CH})_2 \cdot \text{CuMe}$ (X = C, Si or Ti).⁸⁶ In these complexes, CuMe even donates electrons to the π -ligand.

The Cu(I)–($\text{C}\equiv\text{C}$) [or Cu(I)–($\text{C}=\text{C}$)] bonding in copper(I) chloride π -complexes leads to deformation of the tetrahedral environment about the metal atom characteristic of Cu(I) σ -compounds toward the trigonal pyramid and even toward the planar triangle.^{87,88} Deformation of coordination polyhedra is associated with the appearance of a deficiency of electron density in the $d_{x^2-y^2}$ orbital[†] due to its interaction with antibonding MOs of the multiple carbon–carbon bond. In contrast, the d_{z^2} orbital, which is directed toward the axial ligand (for example, Cl_{ax}), possesses residual electron density. Hence, the interaction of Cu(I) with the multiple carbon–carbon bond is accompanied both by shortening of the bonds between the copper atom and the ligands located in the base of the pyramid and by elongation of the $\text{Cu}-\text{L}_{\text{ax}}$ bond, *i.e.*, the Cu(I) atom moves toward the base of the polyhedron. The more efficient the dative component of the π -bond, the more substantial the deformation, the distance from the Cu atom to the midpoint of the multiple carbon–carbon bond ($\text{Cu}-\text{C}^*$) being also shorter due to the synergism of the $\text{Cu(I)} \leftarrow \text{L}$ and $\text{Cu(I)} \rightarrow \text{L}$ components. Knowing the parameters of the coordination unit, such as the $\text{Cu}-\text{C}^*$ distance, the $\text{Cu}-\text{X}_{\text{ax}}$ bond length (X_{ax} is the axial Cl or Br atom), the sum of the LCuL angles ($\sum \text{LCuL}$) in the base of the polyhedron, which characterises the deviation of the metal atom from the equatorial plane,[‡] and

[†] The $d_{x^2-y^2}$ and d_{z^2} orbitals in the initial tetrahedral ligand field after the removal of degeneracy are characterised by lower energies than the remaining three orbitals of d_e symmetry.⁸⁹

[‡] The sums of the LCuL angles equal to 329.5° and 360° correspond to two limiting cases, *viz.*, to the ideal tetrahedron and planar triangle.

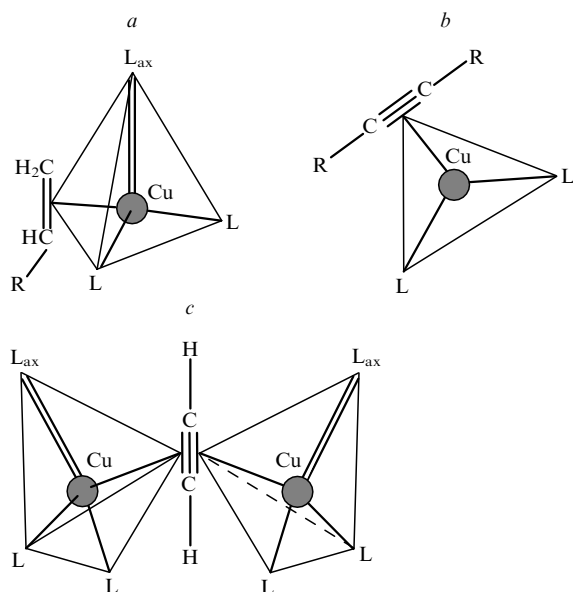


Figure 8. Modes of coordination in the π -complexes of CuCl and CuBr; (a) the trigonal pyramid typical of the Cu(I) atom π -coordinated by the C=C bond; (b) the planar-trigonal environment of Cu(I) in π -complexes with disubstituted acetylene derivatives; (c) the bridging π -coordination of the C≡C bond to the Cu atoms in π -complexes of C₂H₂ and its monosubstituted derivatives.

the length of the π -coordinated multiple carbon–carbon bond, one can assess the state of the C≡C (or C=C) group π -activated on the metal centre and the efficiency of the Cu(I)–(C≡C) [Cu(I)–(C=C)] interaction. The above-mentioned parameters for a series of molecular and anionic copper(I) chloride π -complexes are given in Tables 6–8.

To reveal the differences in the behaviour of the C≡C and C=C bonds with respect to Cu(I), let us consider the data on the alkenyne π -complexes of CuCl and CuBr (Table 7). In the structures of alkenyne complexes **30–37**, the coordination environment about the Cu(I) atom, which is π -coordinated to the C=C bond, is most often a tetrahedron slightly deformed toward the trigonal pyramid (Fig. 8a). The complexes **34** and **35** contain conjugated alkenyne ligands. However, the Cu(I) coordination polyhedron in the complex **34** is more similar to the tetrahedron than that in the complex **35**. In the structure of **35**, the C=C groups interact more efficiently with Cu(I) due to the involvement of the C≡C bond in π -coordination of the metal atom. The distances from the copper atom to the midpoint of the C=C (Cu–C*) bond in the complexes **30–37** are in the range of 1.951(7)–2.00(4) Å, which indicates that the efficiency of the π -bonding is smaller than that of Cu–(C≡C). In particular, the Cu–C*(C=C) distances in the complex **35** are 1.951(7) and 1.962(7) Å, whereas the Cu–C*(C≡C) contact is substantially shorter [1.910(6) Å]. More substantial differences are observed in the structure of **36** in which the multiple bonds of the ligand are isolated [the Cu–C*(C=C) and Cu–C*(C≡C) bonds are 1.97(1) and 1.86(1) Å, respectively]. In this complex, the metal atom coordinated by the C≡C bond is in a planar-trigonal environment (Fig. 8b), whereas the Cu atoms coordinated by the C=C bond are in a trigonal-pyramidal environment. In the copper(I) bromide complexes **33** and **37a,b**, the corresponding geometric parameters of the coordination π -units differ only slightly from each other due to steric hindrances caused by the bulkier bromine atoms. In the complex **32**, the geometric characteristics of the Cu(I) polyhedra formed with the participation of the C≡C or C=C groups are also only slightly different, which suggests that the π -interactions of these bonds with the metal atom are virtually identical in efficiency. To put it differently, the efficiency of π -coordination of the C≡C bond decreases due to

the presence of the phenyl substituent giving rise to steric hindrances. On the whole, the Cu(I) atoms in alkenyne π -complexes tend to interact predominantly with the C≡C bond.

The affinity of alkyne ligands for Cu(I) is particularly pronounced both in molecular and anionic copper(I) halide π -complexes (**24–27** and **38–42**; Tables 6 and 8). If the C≡C group of the alkyne is coordinated only to one Cu atom, the environment of the latter is exclusively planar-trigonal (Fig. 8b). In this case, very short Cu–C*(C≡C) distances [1.886(4)–1.92(1) Å] are observed, which is indicative of efficient interactions (compounds **25**, **26** and **38–42**). In the compounds **24** and **27**, the Cu–C*(C≡C) distances are 1.941(4) and 1.946(6) Å, respectively. Efficient π -interactions in the complexes **24** and **27** are hindered by the phenyl group at the C≡C bond and the bridging character of the octadiyne molecule, respectively.

The propargyl alcohol molecules in the molecular (**28**) and anionic (**29**) π -complexes and the vinylacetylene molecule in the compound **30** whose terminal C≡C group acts as a bridging π -ligand simultaneously coordinated to two metal atoms (Fig. 8c), exhibit peculiar behaviour with respect to Cu(I). One of two copper atoms of the Cu(I)–(C≡C)–Cu(I) unit is always located somewhat closer to the midpoint of the triple bond. If the coordination polyhedra of Cu(I) in the complexes **28–30** are arranged in order of increasing Cu–L_{ax} distances, it can be readily seen that the deformation of the Cu coordination polyhedra from the virtually regular tetrahedron [Cu–L_{ax}, 2.416(2) Å] to the trigonal pyramid [Cu–L_{ax}, 2.605(5)–3.058(7) Å] and then to planar-trigonal coordination [Cu–L_{ax}, 3.738(6) Å] is accompanied by a corresponding shortening of the Cu–C*(C≡C) distance, which indicates an increase in the efficiency of π -bonding in the series under consideration.

The triple bond in the π -complexes of acetylene (**17–23**; Table 6), as in the above-considered complexes **28–30**, is coordinated simultaneously to two metal atoms (Fig. 8c). This coordination is retained both in molecular and anionic compounds. In the structures of the compounds **17–23**, the Cu–C* distances are noticeably longer than those in alkyne and alkenyne π -complexes and are similar to the Cu(I)–(C=C) distances. The average Cu–C* distance in the molecular π -complexes of acetylene **17** (see Fig. 6) and **18** [1.97(2)–2.29(9) Å] is noticeably larger than those in the anionic compounds **20–23** [1.89(2)–1.957(5) Å]. The latter compounds are characterised by virtually planar-trigonal environments about the metal atom.

Therefore, the C≡C group is more prone to interaction with Cu(I) than the C=C group even if the former occupies a position inside the ligand, which is less favourable for coordination to the metal atom. To account for this fact, let us use the data on the electron-donating and electron-withdrawing properties of the ethylene and acetylene molecules and the C₂H₂ molecule π -coordinated to Cu(I).

It is known that acetylene in the ground state exhibits the weaker electron-donating properties (two HOMOs have lower energies) and the weaker electron-withdrawing properties (two LUMOs have higher energies) compared to ethylene.^{13,90} However, in the case of *cis*-distortion of the alkyne molecule in the coordination sphere about the metal atom, the degeneracy of the MOs is removed. As a result, the energies and geometric parameters of the frontier MOs of the alkyne change and it becomes both a better electron-acceptor and electron-donor than alkene. Therefore, the more efficient Cu(I)–(C≡C) π -interaction results from the presence of two π -MOs in the alkyne molecule, which are split into MOs with different energies ($\pi_{||}$ and $\pi_{\perp}$), as well as from the stronger *cis*-distortion of the molecule compared to that of alkenes.

Due to the presence of two MOs in the alkyne, it can interact with Cu(I) and other metals as a bridging ligand and can coordinate two Cu(I) atoms. In this case, as mentioned above, the Cu–C* distances in the Cu(I)–(C≡C) π -units are noticeably shorter than those in the Cu(I)–(C≡C)–Cu(I) π -units, which indicates that the efficiency of the π -interaction in the first case is

higher. This fact is in agreement with the general regularities of coordination chemistry according to which the bond between a bridging μ -L ligand and the metal atom is always weaker than that with the participation of the terminal ligand. This also takes place in the cases of μ -Cl, μ -Me, μ -CO and μ -C₂H₂. In particular, this fact can be explained as follows: if each π -MO of alkyne acts independently (as alkene), two π -MOs, which are weaker π -donors than the highest $\pi_{||}$ -MO of acetylene in the nonbridging π -complex, are involved in bonding. It is also possible that $\pi_{||}$ -MO as well as $\pi_{\perp}^+$ -MO and $\pi_{\perp}^*$ -MO are involved in the formation of the coordination bond in the Cu(I)–(C $\equiv$ C) units.⁹¹ However, this question calls for special investigation.

The efficiency of the interaction between Cu(I) and the multiple carbon–carbon bond affects not only the distance from Cu(I) to the midpoint of the Cu–C* bond, which is determined by the contribution of the donor-acceptor component, but also the length of the coordinated bond determined predominantly by the dative component. The data in Tables 6–8 demonstrate that the smaller the difference in the Cu–C distances (δ), the longer the C $\equiv$ C or C=C bond. Thus, two crystallographically independent C₂H₂ ligands in the crystal of the compound **21a** (Fig. 9) differ in the C $\equiv$ C bond length [1.25(1) and 1.32(2) Å]. This is indicative of the higher and lower efficiency of the corresponding dative components of the Cu(I)–(C $\equiv$ C) π -interactions. In the second case [the coordination unit with the participation of the C(1) $\equiv$ C(1') bond], the asymmetry of the Cu–C bonds is absent, whereas the less elongated C(2) $\equiv$ C(2') bond is located somewhat asymmetrically with respect to the Cu atom [$\delta = 0.03(1)$ Å], which decreases the efficiency of the dative Cu(I)–C(2) $\equiv$ C(2') interaction. This tendency was revealed for a rather large number of examples. However, the C $\equiv$ C bond in the Cu(I)–(C $\equiv$ C) π -unit of the compound **36** is not elongated [1.18(2) Å] in spite of the total symmetry of the Cu–C distances ($\delta = 0$ Å), although the

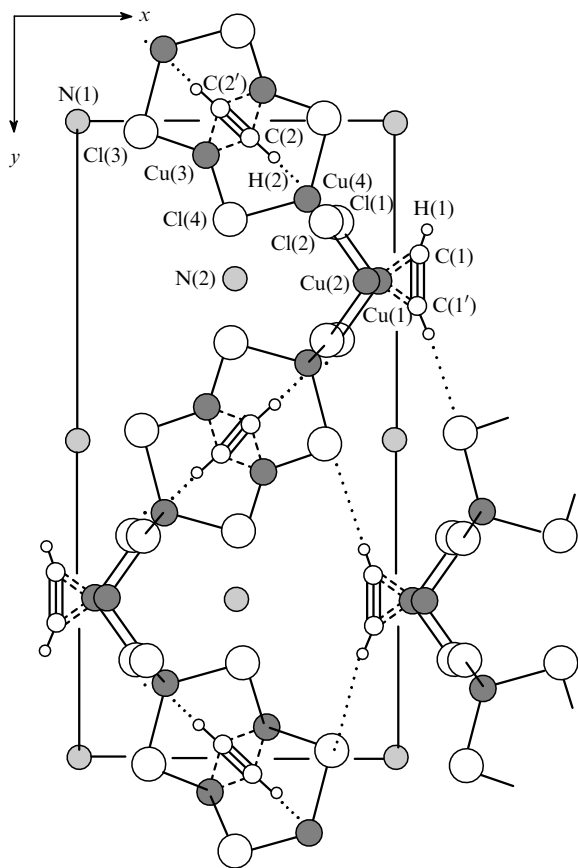


Figure 9. Projection of the structure of NH₄Cu₃Cl₄(HC $\equiv$ CH) (**21a**) onto the *xy* plane.

Cu–C* distance [1.86(1) Å] is indicative of a substantial charge transfer $M \leftarrow L$ increasing the degree of ionicity of the bond.

In most of the structurally studied Cu(I) π -complexes, the terminal carbon atom of the terminal C=C bond is generally located somewhat closer to the Cu atom, whereas the coordinated inner C $\equiv$ C bond in alkyne and alkenyne ligands is most often symmetrical with respect to the Cu atom. Apparently, the inner C $\equiv$ C bond is more stable to the shift with respect to the Cu–C* axis than the C=C bond due to the presence of two π -MOs in the former case. However, the C $\equiv$ C group in CuCl π -complexes with terminal alkynes is characterised by a high tendency to form the asymmetrical Cu(I)–(C $\equiv$ C) π -unit primarily due to the formation of $\equiv$ C–H $\cdots$ Cl hydrogen bonds with the participation of the terminal H atom.

Acetylene and its monosubstituted derivatives are characterised by high CH-acidity.⁹⁰ The dipole moment (μ) of the C–H bond in acetylene is 1.0 D. The positive charge of the dipole is localised on the H atom (the same direction of the dipole of the =C–H bond is observed in alkenes; however, μ for alkenes is approximately 0.6 D). The acidity of the C–H bond in alkynes increases upon the formation of π -complexes with Cu(I) and some other metals. Due to polarisation of the C δ^- –H δ^+ bond, π -complexes become strong acids, which can dissociate to form acetylide compounds depending on pH of the solution. The tendency for dissociation is associated not only with polarisation of the C–H bond, but also with the high stability of coordination products of the resulting RC $\equiv$ C $^-$ anions with Cu(I).^{4,13} At the same time, polarisation of the C–H bond in π -complexes is favourable for hydrogen bonding with the chloride ion or the coordinated chloride ligand. Thus, acetylene or its monosubstituted derivatives in strongly acidic media form π -complexes with CuCl. In these complexes, $\equiv$ C–H $\cdots$ Cl hydrogen bonds exert a stabilising effect on the structures of the compounds.^{92,93} The energies of the hydrogen bonds of this type are comparable with that of the π -interaction [$E_{C-H\cdots Cl} \sim 20$ kJ mol $^{-1}$; $E_{Cu(I)-(C\equiv C)} \sim 50$ kJ mol $^{-1}$]. In structures of π -complexes with acetylene, the $\equiv$ C–H $\cdots$ Cl contacts cause additional polarisation of the Cu–Cl bonds, thus being favourable for strengthening of the π -bonding in the Cu(I)–(C $\equiv$ C)–Cu(I) unit,¹⁷ which is, in turn, reflected in the geometry of the π -coordinated C $\equiv$ C bond. Moreover, there is a particular relationship between elongation of the coordinated C $\equiv$ C bond and the length of the $\equiv$ C–H $\cdots$ Cl hydrogen bond. Thus elongation of the triple bond is accompanied by weakening of the corresponding C(H) $\cdots$ Cl contact. An increase in the C $\equiv$ C bond length due to weakening of the donor-acceptor interaction and strengthening of the dative interaction leads to a decrease in polarisation of the C–H bond and weakening of the hydrogen bond. On the contrary, a smaller elongation of the triple bond due to the stronger donor-acceptor interaction and an increase in polarisation of the C–H bond results in a stronger hydrogen bond and shortening of the H $\cdots$ Cl distance. The electron-withdrawing chlorine atoms, in turn, can substantially affect polarisation of the C–H bonds of the π -coordinated acetylene molecule due to the C(H) $\cdots$ Cl interaction. Thus the stronger the C(H) $\cdots$ Cl hydrogen bond, the higher the degree of polarisation of the $\equiv$ C δ^- –H δ^+ bond. In other words, the formation of the C–H $\cdots$ Cl hydrogen bond enhances the donor-acceptor interaction, which, in turn, strengthens the hydrogen bond. The scheme of action of the $\equiv$ C–H $\cdots$ Cl hydrogen bonds in the structures of copper(I) chloride π -complexes of C₂H₂ is shown in Fig. 10.

The characteristics of the $\equiv$ C–H $\cdots$ Cl hydrogen bonds in the structures of CuCl π -complexes with acetylene and its monosubstituted derivatives are graphically represented in Fig. 11. According to the criteria reported in a study,⁹⁴ the C–Cl distances indicate the existence of a hydrogen bond. It can be seen from the plot that there is a linear correlation between the elongation of the π -coordinated C $\equiv$ C bond and the H $\cdots$ Cl distance. However, this is true only for π -complexes (anionic and molecular) in the structures of which the C $\equiv$ C bond of the ligand molecule acts a

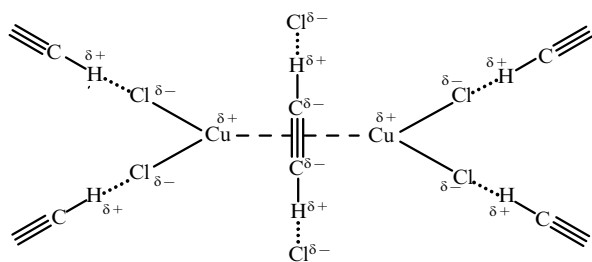


Figure 10. Scheme of $\equiv\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bonds in the structures of copper(I) chloride π -complexes of acetylene.

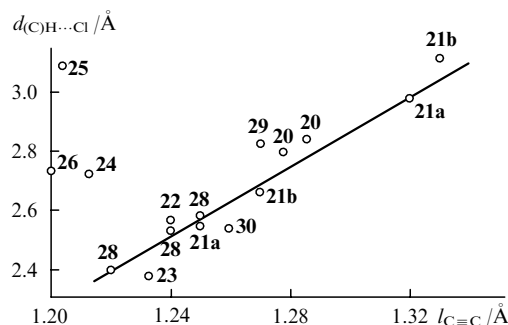


Figure 11. Correlation between the $(\text{C})\text{H}\cdots\text{Cl}$ distance and the $\text{C}\equiv\text{C}$ bond lengths in CuCl π -complexes with acetylene and its monosubstituted derivatives (the linear correlation coefficient $r = 0.85$).

bridge to form the $\text{Cu(I)}-(\text{C}\equiv\text{C})-\text{Cu(I)}$ π -unit. The complexes **24–26** are exceptional (see Fig. 11) due to the formation of the $\text{Cu(I)}-(\text{C}\equiv\text{C})$ π -unit in which the π -interaction characteristic of nonbridging π -complexes prevails. Against its background, the polarising effect of the $\equiv\text{C}-\text{H}\cdots\text{Cl}$ contact is less significant.

Hydrogen bonds play an important role in the structures of the anionic π -complexes **20** and **21a**. In the complex **20**, the lengths of the hydrogen bonds between the hydrogen atoms of two crystallographically independent C_2H_2 molecules and the chlorine atoms are virtually equal [2.85(8) and 2.80(9) Å]. In the structure of **21a**, these bonds are substantially different [2.98(12) and 2.55(12) Å] due to which the π -coordinated triple bond of one C_2H_2 molecule is substantially elongated [1.32(2) Å] compared to the second bond [1.25(1) Å]. In the structure of **20**, the parameters of the π -coordinated triple bond are virtually identical [1.28(1) Å] and correspond to the average value for the two limiting $\text{C}\equiv\text{C}$ bond lengths in the structure of **21a**. In these isostoichiometric complexes, the differences are observed not only in the geometric parameters of the crystallographically independent π -coordinated units, but also in the symmetry of their unit cells due to the different effect of the $\equiv\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bonds. The structures of the complexes **20** and **21a** contain structurally similar (but not identical) $(\text{Cu}_4\text{Cl}_4)_n$ chain fragments (Fig. 12). Thus, all units of the chain in the structure of **20** have the symmetry 2 (Fig. 12b), whereas the Cu_4Cl_4 units in the chains of the structure of **21a** are characterised by the symmetry 2 and m (Fig. 12a). Apparently, this effect caused by the replacement of the K^+ ions by the NH_4^+ ions results from the $\text{NH}_4^+\cdots\text{Cl}^-$ interaction. Thus the ammonium cation's adopting the tetrahedral configuration forms $(\text{N})\text{H}\cdots\text{Cl}$ hydrogen bonds [2.20–2.87(9) Å], which is favourable for the formation of the crystal structure of the complex **21a**, which differs from the crystal structure of the complex **20**. Therefore, the competition of two interactions, viz., $\text{M}^+\cdots\text{Cl}^-$ and $\equiv\text{C}-\text{H}\cdots\text{Cl}$, rather than the $\equiv\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bond affects the geometry of the π -coordinated $\text{C}\equiv\text{C}$ bond in the C_2H_2 molecule in the anionic complexes. In the anionic CuCl π -complexes with acetylene and its monosubstituted derivatives, the efficiency of the $\text{Cu(I)}-(\text{C}\equiv\text{C})$ π -interaction depends on the

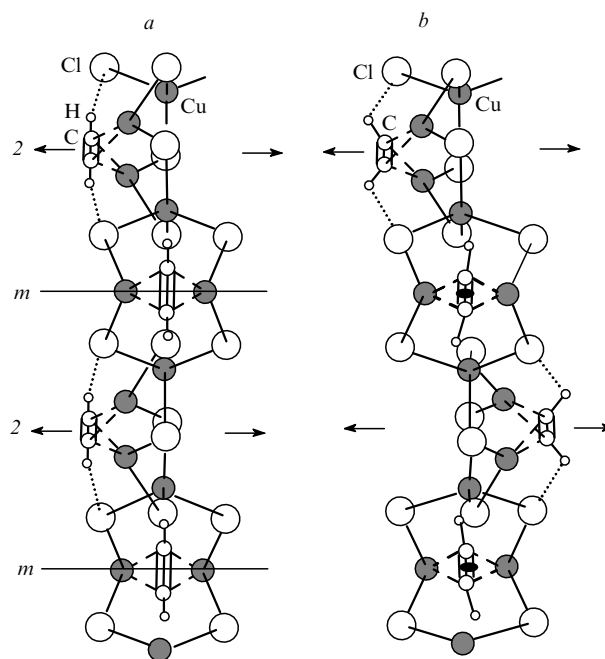
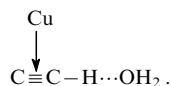


Figure 12. Chain fragments $(\text{Cu}_4\text{Cl}_4)_n$ in the structures of the complexes $\text{NH}_4\text{Cu}_3\text{Cl}_4(\text{HC}\equiv\text{CH})$ **21a** (a) and $\text{KCu}_3\text{Cl}_4(\text{HC}\equiv\text{CH})$ **20** (b).

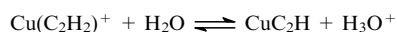
efficiency of $\equiv\text{C}-\text{H}\cdots\text{Cl}$ hydrogen bonding whose strength is determined by the type of the outer-sphere M^+ cation (cations of alkali metals, ammonium or protonated amines). In the case of soluble anionic π -complexes, hydrogen bonding can also occur if the bridging or terminal chlorine atoms forming the coordination polyhedra occupy convenient positions. Weak hydrogen bonds between the NH_4^+ ion and the terminal Cl atoms can also exist. The possibility of hydrogen bonding with the participation of water molecules is also beyond question



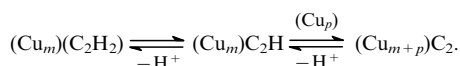
In this connection, the role of the M^+ cations as a component of the Nieuwland catalyst ($\text{MCl}-\text{CuCl}-\text{H}_2\text{O}$) becomes apparent.

2. Acetylenide (ethynyl) complexes of copper(I)

As mentioned above, the formation of ethynyl compounds (compounds possessing at least one $\text{M}-\text{C}\equiv$ bond) in protophilic media (or in the presence of bases) is a characteristic feature of the reactions of acetylene and monosubstituted alkynes with Cu(I) complexes. The polarisation of the $\equiv\text{C}-\text{H}$ bond in Cu(I) π -complexes is substantial and the strength of the resulting $\text{Cu}-\text{C}\equiv$ bond is so high that the Cu^+ ion reacts with C_2H_2 to form $\text{CuC}\equiv\text{CH}$ even in strongly acidic media in the $\text{Cu}_2\text{SO}_4-\text{H}_2\text{SO}_4$ system (up to $[\text{H}_2\text{SO}_4] = 20\% - 25\%$). This reaction is accompanied by the formation of vinylacetylene in small amounts.⁹⁵

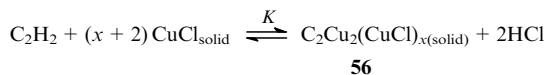


Studies of the formation of the so-called 'yellow' complexes in the reactions of C_2H_2 with solutions of $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ polynuclear anions by spectrophotometric and potentiometric methods demonstrated that the following equilibria occur in solutions at 25–80 °C depending on the acidity of the medium⁵⁸

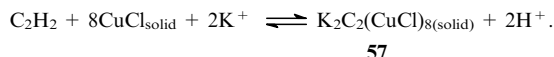


By increasing the acidity of the medium, one can go from symmetrical acetylenide $(\text{Cu}_m)_p(\text{C}_2^{2-})$ to unsymmetrical $(\text{Cu}_m)(\text{C}_2\text{H}^-)$ and again to the $(\text{Cu}_m)(\text{C}_2\text{H}_2)$ π -complex.

The formation of solid acetylenide complexes containing Cu_2C_2 has been thoroughly studied by Vestin.⁹⁶ In particular, the equilibrium constant of the formation of the 'violet' complex **56** ($K = a_{\text{HCl}}^2/p_{\text{C}_2\text{H}_2} = 4$ at 25 °C) was measured



and the composition of the 'yellow' solid complex **57** was established



It was concluded⁹⁶ that the solution of the $\text{CuCl}-\text{KCl}-\text{H}_2\text{O}$ system contains the $[\text{C}_2(\text{CuCl})_m]^{2-}$ anion. Unsymmetrical ethynyl complexes in solutions⁵⁸ $\{[\text{HCl}] = 0.05-0.6 \text{ } \tilde{m}, \text{ the acidity of the medium } (h_0) \text{ is } 0.2-5, \text{ pH} = 1.1-0.0\}$ have predominantly the compositions $[\text{Cu}_4\text{Cl}_4(\text{C}\equiv\text{CH})]^-$ and $[\text{Cu}_4\text{Cl}_5(\text{C}\equiv\text{CH})]^{2-}$.

Recently, ethynyl complexes and acetylenide complexes of copper(I) chloride have been synthesised and their structures have been studied (see Table 9 and references therein). These studies provided convincing evidence that unsymmetrical polynuclear ethynyl complexes $[\text{Cu}_m\text{Cl}_n(\text{C}\equiv\text{CR})]^{(n-m+1)-}$ do exist. New structures, which have not been described previously for non-halide complexes, were revealed.⁹⁷⁻¹¹⁶

In the case of acetylene, the $(\text{ImH})_4\text{Cu}_9\text{Cl}_{11}(\text{C}\equiv\text{CH})_2$ (**43**)⁴⁵ and $(\text{PyH})_4\text{Cu}_9\text{Cl}_{12}(\text{C}\equiv\text{CH})$ (**44**)³⁹ compounds were obtained as insoluble (crystalline) acetylenide complexes. In these complexes, the $\text{C}\equiv\text{CH}$ group is bridging and is coordinated to the copper atoms only through one α -carbon atom (the μ - η^1 -, η^1 - $\text{C}\equiv\text{CH}$ - or σ , σ -modes of coordination) (Fig. 13). The $\text{C}\equiv\text{C}$ bond lengths in these complexes are 1.21(2) and 1.19(7) Å, respectively, and the $\text{Cu}-\text{C}$ bond lengths are 1.97(1) and 1.92(3) Å, respectively. This type of the ligand is rather often observed in ethynyl complexes of the $\text{Cu}_2(\text{C}\equiv\text{CR})_2\text{L}_4$ ($\text{L} = \text{PR}_3$) type.⁹⁷ For simplicity, these

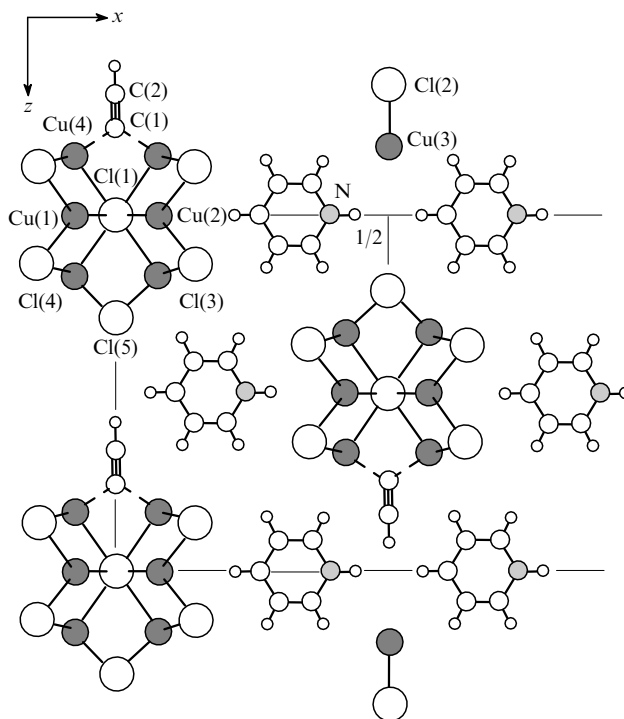


Figure 13. Projection of the structure of $(\text{PyH})_4\text{Cu}_9\text{Cl}_{12}(\text{C}\equiv\text{CH})$ (**44**) onto the xz plane (one layer is shown).

ethynyl compounds will be called σ -complexes. The complex **43** contains the $\text{Cu}_4\text{Cl}_5(\text{C}_2\text{H})^{2-}$ anion. In the acetylenide complex $(\text{NH}_4)_8\text{Cu}_{29}\text{Cl}_{29}(\text{C}\equiv\text{C})_4 \cdot 7\text{H}_2\text{O}$ (**45**), the C_2^{2-} anion, unlike the C_2H^- anion, is coordinated both in the η^1 - and η^2 -modes (σ , π -mode) and serves as a bridge between eight copper atoms (Fig. 14). In the structure of **45**, two crystallographically independent C_2^{2-} species are present. Each of these species acts as a

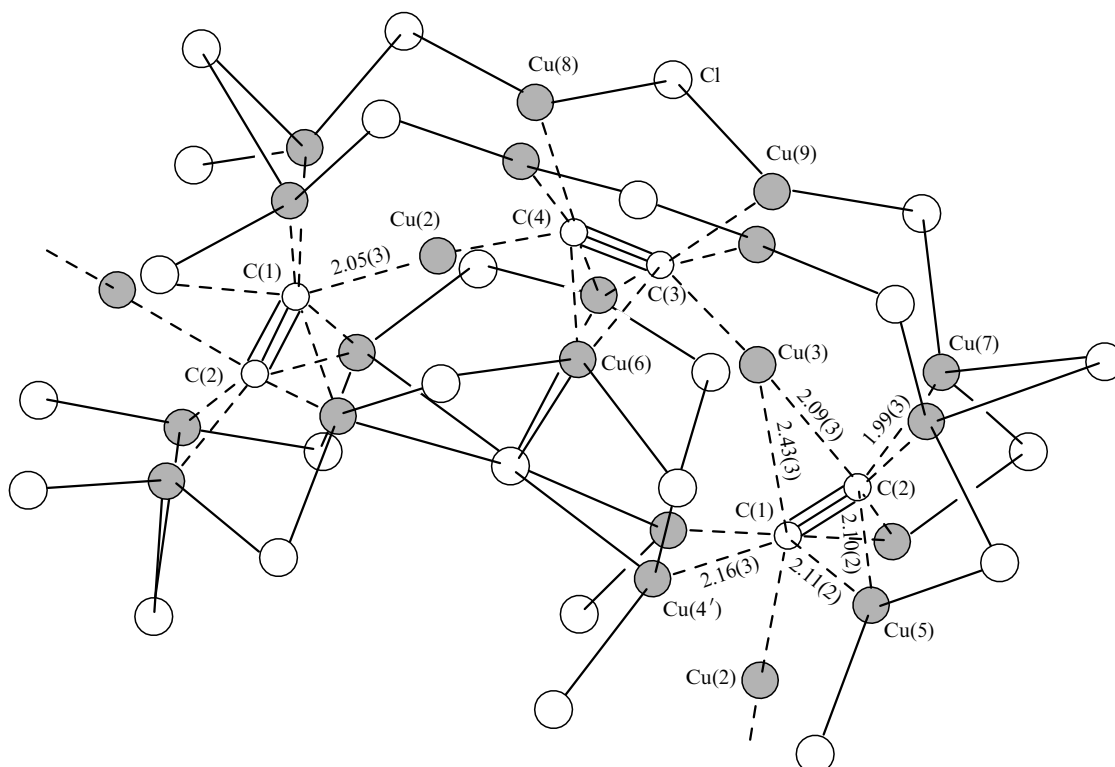


Figure 14. Fragment of the structure of the $(\text{NH}_4)_8\text{Cu}_{29}\text{Cl}_{29}(\text{C}\equiv\text{C})_4 \cdot 7\text{H}_2\text{O}$ complex (**45**). The distances from the $\text{Cu}(3)$ and $\text{Cu}(5)$ atoms to the midpoint of the $\text{C}(1)-\text{C}(2)$ bond are 2.18(3) and 2.01(2) Å, respectively.

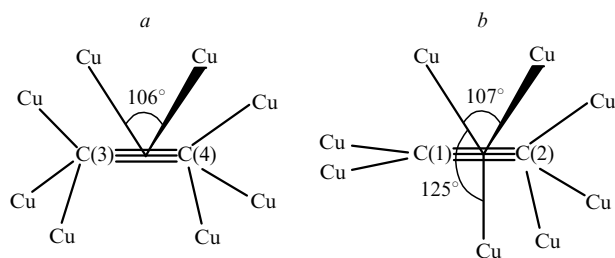
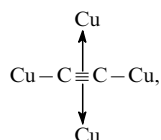


Figure 15. π,σ -Coordination units in the structure of the $(\text{NH}_4)_8\text{Cu}_{29}\text{Cl}_{29}(\text{C}\equiv\text{C})_4\cdot 7\text{H}_2\text{O}$ complex (**45**).

bridging σ,π,σ -ligand, which coordinates simultaneously eight metal atoms. Noteworthy are the modes of coordination of the Cu(I) atoms by two independent C_2^{2-} species. Each of two carbon atoms of the $\text{C}(3)\equiv\text{C}(4)$ group forms σ -bonds with three copper atoms (Fig. 15 *a*). Therefore, the $\text{C}(3)\equiv\text{C}(4)$ group is coordinated in the $\mu_3\text{-}\eta^1,\eta^1,\eta^1,\mu_2\text{-}\eta^2,\eta^2,\mu_3\text{-}\eta^1,\eta^1$ -mode, *i.e.*, this group acts as the σ,π,σ -ligand. The effect of six copper(I) atoms η^1 -coordinated to the C_2^{2-} ion and two copper atoms η^2 -coordinated to the same ion on the $\text{C}\equiv\text{C}$ bond is so high that the geometry of the η^2 -unit changes and the $\text{Cu}-\text{C}^*-\text{Cu}$ angle reaches 106° . In this case, the $\text{C}(1)\equiv\text{C}(2)$ bond can additionally coordinate the third copper atom (Fig. 15 *b*). Apparently, the unusual mode of coordination to the copper(I) atoms is the characteristic feature of the C_2^{2-} anion. Thus the perfectly planar coordination σ,π,π,σ -unit



was found in the structure of the complex $[\text{Cu}_4(\text{Ph}_2\text{PCH}_2\text{PPh}_2)_4(\text{C}\equiv\text{C})](\text{BF}_4)_2\cdot 4\text{Me}_2\text{CO}$.¹¹⁷ In this unit, the $\text{Cu}-\text{C}^*-\text{Cu}$ angle is 180° . Apparently, the structure of the 'yellow' complex studied by Vestin⁹⁶ also contains the fragments (*a*) and (*b*) (see Fig. 15). The σ,π -coordination of several copper atoms by the C_2^{2-} group gives rise to clusters in which the shortest $\text{Cu}\cdots\text{Cu}$ distance is $2.452(6)$ Å. Coordination of the ethynyl ligand to three copper(I) atoms ($\mu_3\text{-}\eta^1,\eta^1,\eta^1\text{-C}\equiv\text{C}$) to form the trinuclear cluster is also very typical of ethynyl complexes.⁹⁷ The question about the nature of the η^2 -bonds between the $\text{C}\equiv\text{C}$ group and three metal atoms deserves special analysis.

Structural motifs found in ethynyl complexes containing $\text{RC}\equiv\text{C}$ groups are widely diversified. The efficiency of η^2 -coordination of the Cu(I) atom by the $\text{RC}\equiv\text{C}$ group depends on the η^1 -mode of coordination. The geometric parameters of the π -coordination units in the structures of the CuCl σ,π -complexes with acetylene and its terminal derivatives [which, according to the criteria used in the previous section of this chapter, characterise the efficiency of the $\text{Cu(I)}-(\eta^2\text{-C}\equiv\text{CR})$ bonding] are given in Tables 9 and 10. It can be readily seen that two metal atoms in the coordination π -unit ($\mu\text{-}\eta^2,\eta^2\text{-C}\equiv\text{CR}$) in cluster ethynyl complexes of copper(I) are located at somewhat different distances from the midpoint of the $\text{C}\equiv\text{C}$ bond, as in the CuCl π -complexes with $\text{HC}\equiv\text{CCH}_2\text{OH}$ and $\text{HC}\equiv\text{CCH}=\text{CH}_2$ [compounds **28** and **29** (see Table 6) and **30** (see Table 7)]. However, shortening of the $\text{Cu}-\text{C}^*$ distance in σ,π -complexes, which is determined primarily by the donor-acceptor component of the π -interaction, unlike that in CuCl π -complexes with $\text{HC}\equiv\text{CCH}_2\text{OH}$ and $\text{HC}\equiv\text{CCH}=\text{CH}_2$, is not accompanied by an increase in the dative transfer, *i.e.*, it does not cause additional deformation of the trigonal-pyramidal environment about the Cu(I) atom. Moreover, the σ,π -complexes are characterised by the following effect: the smaller elongation of the $\text{Cu}-\text{X}_{\text{ax}}$ distance in the coordination π -unit ($\mu\text{-}\eta^2,\eta^2\text{-C}\equiv\text{CR}$) corresponds to the shorter $\text{Cu}-\text{C}^*$ distance due, apparently, to the synergism of the $\text{Cu(I)}-(\eta^1\text{-C}\equiv\text{CR})$ and $\text{Cu(I)}-(\eta^2\text{-C}\equiv\text{CR})$ interactions. Such mutual

Table 10. The CuC^*Cu angles in the π -coordinated Cu(I) units in the structures of π,σ -complexes of CuCl with acetylene and its terminal derivatives.

Complex	CuC^*Cu angle /deg	Cluster type	Ref.
45	125(1)	—	75
	125(1)	—	
	107(1)	—	
	106(1)	—	
46	93.5(6)	II	45
48	95(1)	II	76
49	93.6(9)	II	77
50	97(1)	I	78
51	90.4(7)	IV	52
52	96.9(2)	I	39
	89.8(2)	IV	
53	96.9(6)	III	51
54	98.1(3)	IV	79
55	98(2)	III	66

strengthening of the η^1 - and η^2 -bonds is manifested to a greater or lesser extent depending on the number of the σ -coordinated Cu atoms and their arrangement with respect to the $\text{C}\equiv\text{C}$ group.

In this connection, it is worthwhile to consider the stereochemistry of the $[\text{Cu}_4(\text{C}\equiv\text{CR})]$ and $[\text{Cu}_5(\text{C}\equiv\text{CR})]$ clusters found in the structures of copper(I) chloride σ,π -complexes with terminal derivatives of acetylene. Four major types of cluster were distinguished (see Table 10). The differences in their structures are determined by the difference in the orientation of two mutually perpendicular π -MOs of the ethynyl group of the σ,π -coordinated $\text{C}\equiv\text{CR}$ ligand with respect to the plane *P* passing through the $\text{C}\equiv\text{C}$ bond (Fig. 16). In the structures of the complexes containing clusters of type I, the plane of one of the π -MOs of the $\text{C}\equiv\text{C}$ group (for example, $\pi_{||}$) coincides with the plane *P*, *i.e.*, the π -coordinated C(2) atom and the $\text{C}\equiv\text{C}$ bond together with two σ -bonded Cu(3) and Cu(4) atoms are in a single plane, whereas the normal *mn* to this plane coincides with the axis of another $\pi_{\perp}$ -MO [the $\text{Cu(1)}-\text{C}^*$ axis] (Fig. 16 *a*). Both π -MOs of the $\text{C}\equiv\text{C}$ group ($\pi_{||}$ and $\pi_{\perp}$) in clusters of the types II–IV, unlike those in clusters of type I, are located at an angle of 45° to the normal *mn* (as well as to the plane *P*). [In the case of clusters of the types III and IV (Fig. 16 *c,d*), the plane *P* passes perpendicularly to the normal *mn* to retain the spatial orientation of the π -coordinated copper(I) atoms analogous to that in clusters II (Fig. 16 *b*).] The clusters II, III and IV differ primarily in the orientation of the σ -coordinated Cu atoms. Thus, the σ -coordinated Cu(3) and Cu(4) atoms in clusters of the type II lie in the plane *P* (Fig. 16 *b*). The rotation of these σ -coordinated Cu(3) and Cu(4) atoms about the $\text{C}\equiv\text{C}$ axis by 90° in such a way that they form a new plane (*Q*) with the normal *mn* leads to clusters of the type III (Fig. 16 *c*). The replacement of one σ -coordinated Cu(4) atom by two atoms [Cu(4) and Cu(5)] in such a way that these atoms are no longer located in the plane *Q* [the Cu(4) and Cu(5) atoms are located behind and in front of the plane *Q*, respectively; the Cu(4)C(1)Cu(5) angle $\approx 80^\circ$] gives rise to a cluster of the type IV (Fig. 16 *d*). In addition to the above-considered four cluster types, combined types of clusters are also observed in the structures of Cu(I) σ,π -complexes. An example is the $[\text{Cu}_8]$ cluster in the structure of **52**, which consists of clusters of the types I and IV linked to one another through the bridging Cu atom (Fig. 17). The $[\text{Cu}_9]$ cluster in the structure of **54** is composed of two clusters of the type IV (Fig. 18). Clusters of the types I–IV were found for the first time in ethynyl complexes of copper(I) chloride.

In the structures of σ,π -complexes containing clusters of the type I, the coplanar arrangement of the π - and σ -coordinated metal atoms [for example, the π -coordinated Cu(3) atom and the σ -coordinated Cu(1) and Cu(2) atoms in the structure of **50** (Fig. 19)] and the $\text{C}\equiv\text{C}$ bond leads to the mutual strengthening

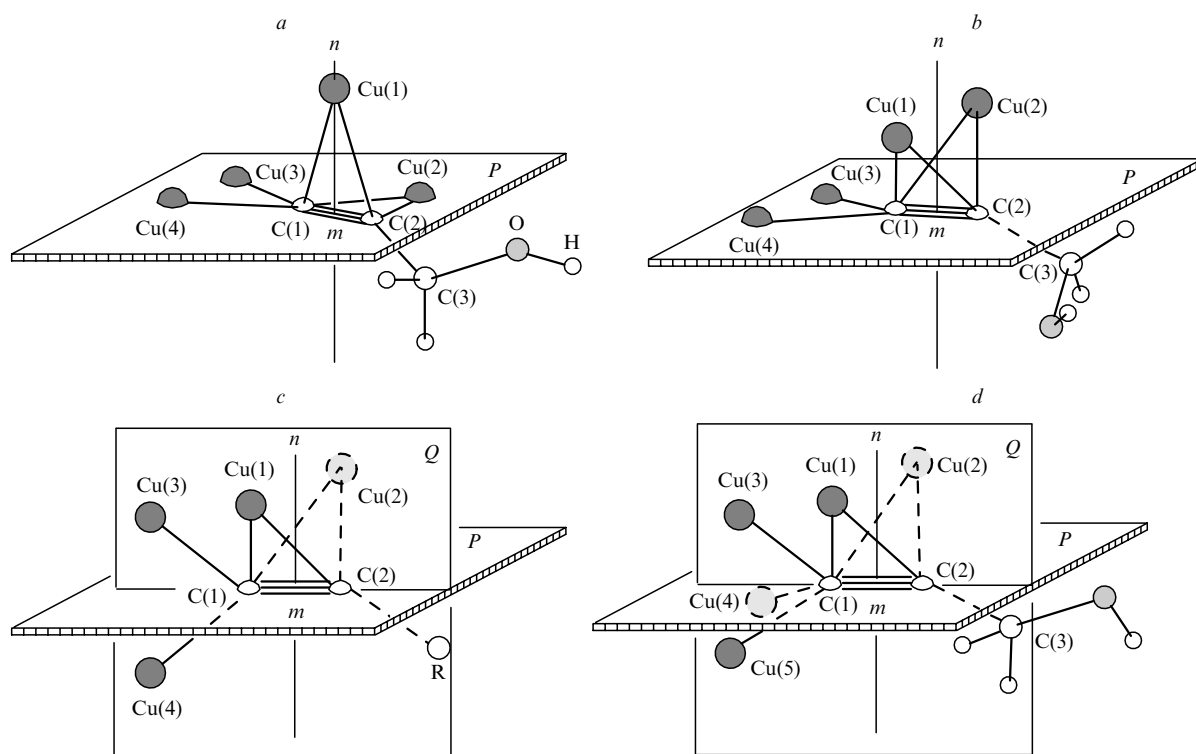


Figure 16. Types of clusters observed in the structures of ethynyl copper chloride complexes: (a) type I {the $[\text{Cu}_4(\text{C}\equiv\text{CCH}_2\text{OH})]$ cluster}; (b) type II {the $[\text{Cu}_4(\text{C}\equiv\text{CCH}_2\text{OH})]$ cluster}; (c) type III {the $[\text{Cu}_4(\text{C}\equiv\text{CR})]$ cluster, where $\text{R} = \text{CH}=\text{CH}_2$ or CH_2OH }; (d) type IV {the $[\text{Cu}_5(\text{C}\equiv\text{CCH}_2\text{OH})]$ cluster}; mn is the normal to the plane P .

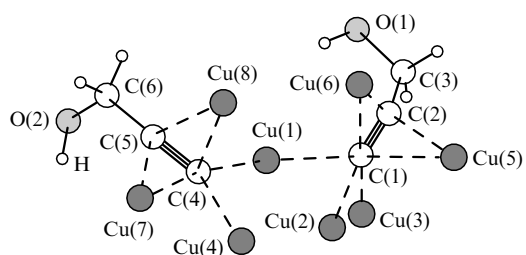


Figure 17. Cluster fragment $[\text{Cu}_8(\text{C}\equiv\text{CCH}_2\text{OH})_2]$ in the structure of $(\text{PyH})_2\text{Cu}_8\text{Cl}_8(\text{C}\equiv\text{CCH}_2\text{OH})_2 \cdot \text{H}_2\text{O}$ (**52**).

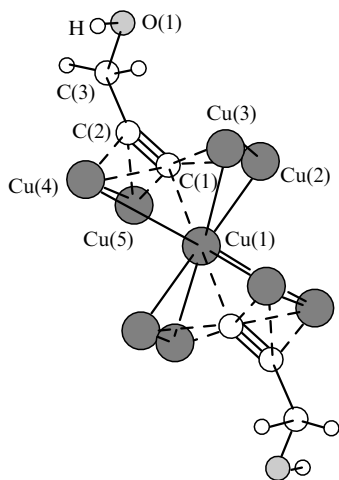


Figure 18. Cluster fragment $[\text{Cu}_9(\text{C}\equiv\text{CCH}_2\text{OH})_2]$ in the structure of $[\text{HO}(\text{CH}_2)_2\text{NH}_3]\text{Cu}_9\text{Cl}_8(\text{C}\equiv\text{CCH}_2\text{OH})_2 \cdot 2\text{H}_2\text{O}$ complex (**54**).

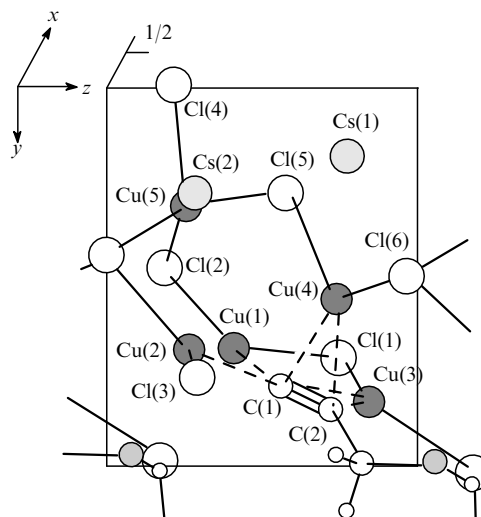


Figure 19. Fragment of the structure of $\text{Cs}_2\text{Cu}_5\text{Cl}_6(\text{C}\equiv\text{CCH}_2\text{OH})$ (**50**).

of two individual types of interactions, *viz.*, the acetylenide and π -interactions. This process becomes so efficient that the coordination polyhedra about the σ - and π -coordinated copper(I) atoms become planar-trigonal (see Tables 9 and 10). Apparently, this synergism occurs due to the angular overlapping simultaneously of three orbitals, *viz.*, the occupied $d_{x^2-y^2}$ orbitals of the σ -[Cu(1)] and π -coordinated [Cu(3)] metal atoms, and the antibonding unoccupied MO (for example, $\pi_{\parallel}^*$) of the acetylene bond. It should be noted that there are spatial prerequisites for this 'three-centre' overlapping in the structure of **50** [the $\text{Cu}(2)\text{C}(1)\text{Cu}(1)$, $\text{Cu}(1)\text{C}(1)\text{Cu}(3)$ and $\text{Cu}(2)\text{C}(1)\text{Cu}(4)$ angles are $81.3(9)^\circ$, $84.2(9)^\circ$ and $89.9(9)^\circ$, respectively]. However, mutual strengthening of the $\text{Cu(I)}-(\eta^1\text{-C}\equiv\text{CR})$ and $\text{Cu(I)}-(\eta^2\text{-C}\equiv\text{CR})$ interac-

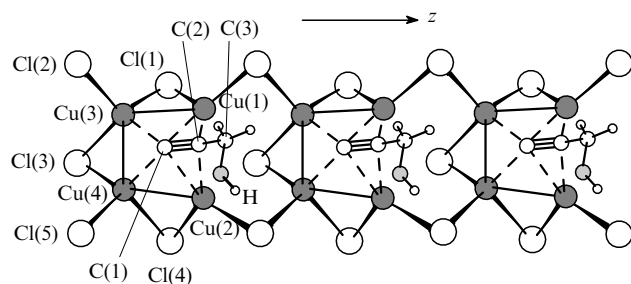


Figure 20. Anion $[\text{Cu}_4\text{Cl}_5(\text{C}\equiv\text{CCH}_2\text{OH})_2]^{2-}$ in the structure of the $(\text{NH}_4)_2\text{Cu}_4\text{Cl}_5(\text{C}\equiv\text{CCH}_2\text{OH})\cdot\text{H}_2\text{O}$ complex (**48**).

tions does not cause the expected substantial elongation of the $\text{C}\equiv\text{C}$ bond in the complex **50** [1.22(3) Å] because the above-described angular dative process causes polarisation of the $\text{C}(1)^{\delta-}\equiv\text{C}(2)^{\delta+}$ bond. Quite a different situation is observed in the case of formation of the cluster of the type II (see Fig. 16*b*). In this cluster, strengthening of two types of interactions (σ and π) is less efficient for geometric reasons because two π -MOs of the alkyne are located at an angle of 45° to the normal mn . As a result, the coordination polyhedra about the σ -coordinated Cu(I) atoms in the structures of **46**, **48** (Fig. 20) and **49** remain tetrahedral, whereas the π -coordinated Cu(I) atoms are characterised by the trigonal-pyramidal environment. In this case, the $\text{C}\equiv\text{C}$ bond is substantially elongated [1.29(1) Å] due to lower polarisation. The considerable synergism of the σ and π interactions is also observed in the complexes **54** (Fig. 21), **53** and **55** (Fig. 22), which contain clusters of the types III and IV (see Figs 16*c,d*). Their π - and σ -coordinated Cu(I) atoms are characterised predominantly by the planar-trigonal environment and the $\text{C}\equiv\text{C}$ bond is virtually not elongated (see Tables 9 and 10).

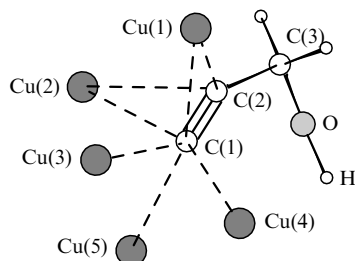


Figure 21. Cluster fragment $[\text{Cu}_5(\text{C}\equiv\text{CCH}_2\text{OH})]$ in the structure of $\text{Rb}_3\text{Cu}_7\text{Cl}_9(\text{C}\equiv\text{CCH}_2\text{OH})\cdot\text{H}_2\text{O}$ (**51**).

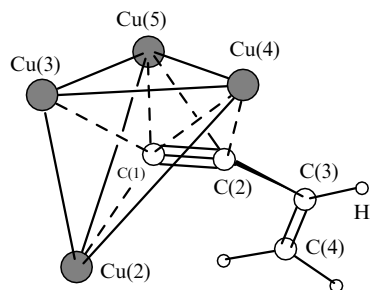


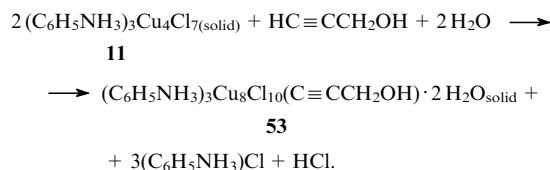
Figure 22. Cluster fragment $[\text{Cu}_4(\text{C}\equiv\text{CCH}=\text{CH}_2)]$ in the structure of $\text{Cu}_{25}\text{Cl}_{17}(\text{C}\equiv\text{CCH}=\text{CH}_2)_8\cdot 14\text{H}_2\text{O}$ (**55**).

3. Structural aspects of formation of some π -complexes and σ -ethynyl derivatives

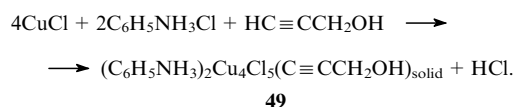
Structures of π -complexes and products of their reversible conversions (σ -complexes) are determined both by the structures of the $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ anions in solution and the stability of the products, *i.e.*, by the favourable formation of a particular struc-

ture. However, the structures of compounds isolated from solution may not be directly associated with the mechanism of their formation because conversions of the initial intermediates of any type lead to the formation of more stable structures, but the least soluble compounds are isolated from solution. Thus, the ethynyl compound with composition $\text{Cu}_m(\text{C}_2\text{H})$ can be formed by the reaction of $\text{Cu}_p(\text{C}_2\text{H})$ with Cu_q ($p+q=m$) in solution. At the same time, it is of interest to analyse possible 'genetic' relations between the structures of the initial copper chloride anions and the products formed in the reactions of the latter with $\text{RC}\equiv\text{CH}$.

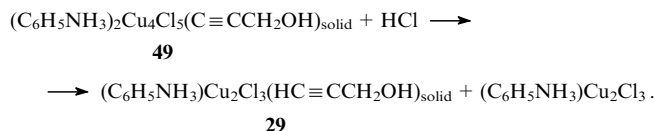
Let us consider the group of crystalline compounds formed in the $(\text{C}_6\text{H}_5\text{NH}_3)\text{Cl}-\text{CuCl}-\text{H}_2\text{O}-\text{HC}\equiv\text{CCH}_2\text{OH}$ system. Colourless crystals of $(\text{C}_6\text{H}_5\text{NH}_3)_3\text{Cu}_4\text{Cl}_7$ (**11**), which precipitated from a concentrated almost neutral solution of CuCl (4 mol) and $(\text{C}_6\text{H}_5\text{NH}_3)\text{Cl}$ (3 mol) in H_2O (20 mol), rapidly dissolved after addition of propargyl alcohol to give yellow crystals of the ethynyl complex **53**.



The reaction was accompanied by a decrease in pH to ~ 1.5 . Under analogous conditions [but when CuCl and $(\text{C}_6\text{H}_5\text{NH}_3)\text{Cl}$ were taken in the molar ratio of 2:1], the complex **49** was obtained.



Unlike the complex **53**, the ethynyl complex **49** was converted into the π -complex **29** upon storage in the mother liquor ($\text{pH} \leq 1$). This fact indicates that the process is non-equilibrium in character.



Let us consider the relationship between the stereochemistry of compounds **11** and **53** and the possible mechanism of formation of the latter in the solid-phase process (Fig. 23). The subunit of the $(\text{Cu}_4\text{Cl}_7^{3-})_n$ anion in the structure of **11**, which consists of the Cu coordination polyhedra linked to each other, is shown in Fig. 23*a*. The molecule of propargyl alcohol can replace the $\mu\text{-Cl}$ atom (which is hatched in Fig. 23*a*) in **11** and can be incorporated into the initial macropolyhedron to form the π -complex ($\eta^2\text{-RC}\equiv\text{CH}$). In this case, the octahedral cavity in the macropolyhedron is transformed into a square-pyramidal cavity. Subsequent deprotonation of the π -ligand with the H_2O molecule affords the expected π -complex with the $\text{C}\equiv\text{CR}$ ligand giving rise to the bridging $\mu\text{-}\eta^2, \mu\text{-}\eta^2\text{-C}\equiv\text{CCH}_2\text{OH}$ ligand (Fig. 23*b*). The formation of the π -complex leads to weakening of some Cu–Cl bonds (indicated by dashed lines in Fig. 23*b*) and to their cleavage accompanied by the formation of two new Cu–C η^1 -bonds (Fig. 23*c*) in the $[\text{Cu}_4(\text{C}\equiv\text{CCH}_2\text{OH})]$ cluster, which is a component of the complex **53**. In the structure of the latter, the $[\text{Cu}_8\text{Cl}_{10}(\text{C}\equiv\text{CCH}_2\text{OH})^{3-}]_n$ anions form layers in which the σ, π -coordinated $\text{C}\equiv\text{CR}$ group of each propargylium anion is clamped between four Cu atoms inside the square-pyramidal cavity. Due to steric hindrance to the penetration of the H_3O^+ ion into the cavity toward the α -carbon atom of the $\text{C}\equiv\text{CCH}_2\text{OH}$ ligand and the high strength of bonding of the σ - and π -coordinated anion [in the structure of **53**, the length of one of the Cu–C bonds of the acetylenide type is 1.89(2) Å and the Cu–C*

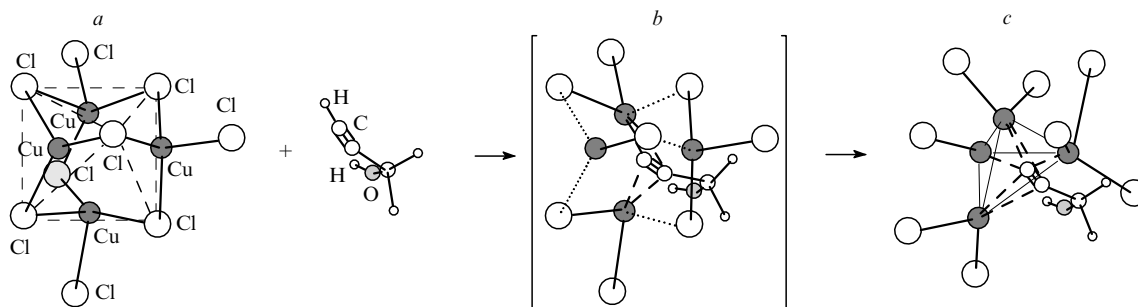


Figure 23. Conversion of the $(\text{C}_6\text{H}_5\text{NH}_3)_3\text{Cu}_4\text{Cl}_7$ complex (**11**) into the $(\text{C}_6\text{H}_5\text{NH}_3)_3\text{Cu}_8\text{Cl}_{10}(\text{C}\equiv\text{CCH}_2\text{OH})\cdot 2\text{H}_2\text{O}$ complex (**53**) in the presence of $\text{HC}\equiv\text{CCH}_2\text{OH}$ (the stereochemical aspect).

distance is 1.97(1) Å], the complex **53** is very resistant to decomposition or conversion into the π -complex under the action of HCl .

The formation of the complex **49** differs from the above-considered complex in the structural features. Judging from the stoichiometry of the formation of the complex **29**, the Cu_2Cl_3^- anion is involved in the formation of the complex **49**. This anion was revealed for the first time in the CsCu_2Cl_3 complex (**5**) (Fig. 24) and its structure differs fundamentally from that of the $(\text{Cu}_4\text{Cl}_7^{3-})_n$ anion. The Cu_2Cl_3^- anion is characterised by the fact that the coordination polyhedra about the Cu atoms are linked to each other exclusively through edges to form infinite $(\text{Cu}_2\text{Cl}_3^-)_n$ chain fragments within which all metal atoms are virtually in a single plane. In this case, a peculiar sequence of planar (approximately square) $n[\text{Cu}_4]$ matrices with $\text{Cu}\cdots\text{Cu}$ contacts [2.81(1) Å]

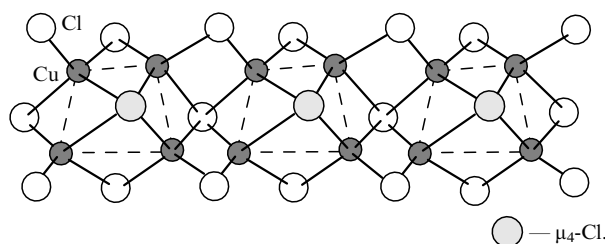


Figure 24. Anion in the structure of the CsCu_2Cl_3 complex (**5**).

appears. In solution, the complex **5** (Fig. 24) produces the Cu_2Cl_3^- anions (**A**), which interact with alkyne to form the π -complex $[\text{Cu}_2\text{Cl}_3(\text{RC}_2\text{H})]^-$ (**B**).

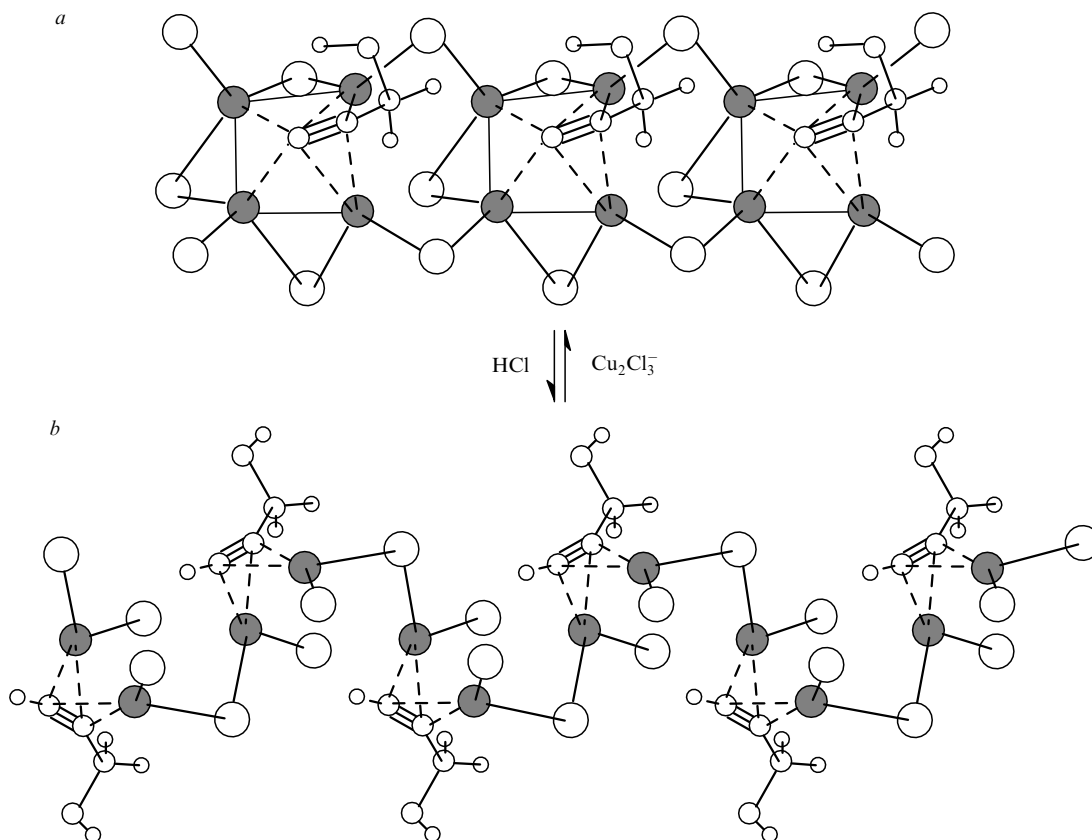
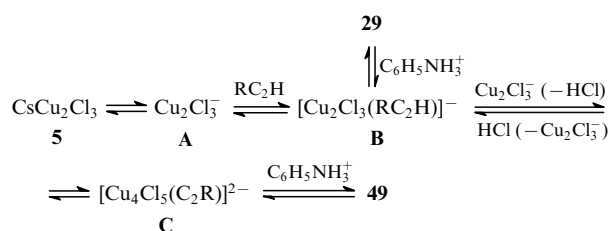


Figure 25. Scheme of formation and conversions of the crystals of the $(\text{C}_6\text{H}_5\text{NH}_3)_2\text{Cu}_4\text{Cl}_5(\text{C}\equiv\text{CCH}_2\text{OH})$ complex (**49**) into $(\text{C}_6\text{H}_5\text{NH}_3)_2\text{Cu}_2\text{Cl}_3(\text{HC}\equiv\text{CCH}_2\text{OH})$ (**29**): (a) the $[\text{Cu}_4\text{Cl}_5(\text{C}_2\text{R})_2]^{2-}_n$ anion; (b) the $[\text{Cu}_2\text{Cl}_3(\text{RC}_2\text{H})]^-_n$ anion.



R = CH₂OH.

The formation of the complex **49** is a non-equilibrium process and is, most likely, determined by the kinetics of its crystallisation. As a consequence, the π -complex **B** rapidly reacts with the Cu_2Cl_3^- ion in solution to yield the ethynyl complex **C**, which precipitates as the compound **49**. The slow reaction of the complex **49** (through the soluble form **C**) with HCl followed by elimination of Cu_2Cl_3^- to form (through the complex **B**) gives rise to the complex **29**, which is thermodynamically more stable under these conditions.

In the $[\text{Cu}_4\text{Cl}_5(\text{C}\equiv\text{CCH}_2\text{OH})]^{2-}$ anion of the compound **49** (Fig. 25a), the α -carbon atom of the $-\text{C}\equiv\text{CCH}_2\text{OH}$ fragment is accessible to attack by the proton. In addition, the bonds between the σ -coordinated Cu atoms and the α -carbon atom in the structure **49** are weaker [the Cu–C $\equiv$ bonds are in the range of 1.95(2)–2.00(2) Å] than those in the complex **53**. Hence, the possibility of the conversion of the $[\text{Cu}_4\text{Cl}_5(\text{C}\equiv\text{CCH}_2\text{OH})]^{2-}$ anion in crystals of the complex **49** accompanied by elimination of the Cu_2Cl_3^- fragments to form the $[\text{Cu}_2\text{Cl}_3(\text{HC}\equiv\text{CCH}_2\text{OH})]^-$ anion of the complex **29** must not be ruled out (Fig. 25b). Crystals of the complex **29** appear in the mother liquor (pH $\leq$ 1) immediately after the disappearance of crystals of the complex **49**.

IV. Catalytic conversions of acetylenic compounds in solutions of copper(I) chloride complexes

Studies of the physicochemical properties of the NH_4Cl – CuCl – H_2O system provided the basis for the development of the procedure for investigation of the kinetics of reactions in concentrated aqueous solutions.^{13,118} The principal results of these investigations are considered below.

1. Kinetics of catalytic reactions of acetylene and its derivatives in concentrated aqueous solutions of MCl–CuCl

In studies of the kinetics of various reactions of acetylene (and its derivatives) in concentrated aqueous solutions of MCl and CuCl, kinetic models are generally constructed¹³ with the use of an empirical dependence of the following type:

$$r = \varphi(p_{\text{C}_2\text{H}_2}, [\text{HCl}]_{\Sigma}, [\text{CuCl}]_{\Sigma}, [\text{NH}_4\text{Cl}]_{\Sigma}),$$

where r is the reaction rate and p is the partial pressure.

If the solution contains polynuclear complexes and does not contain an excess of chloride anions with respect to metal, there is no way to express the concentration of free catalytically active complexes (one or several) in terms of $[\text{CuCl}]_{\Sigma}$ (i.e., to account for the material balance with respect to the catalyst in the kinetic equation). Hence, the only approach to a theoretically justified adequate kinetic model and to the elucidation of the reaction mechanism in these systems consists in measuring the concentrations (or activities) of the free reagents and components of the solution (Cu^+ and Cl^-) under stationary conditions of catalytic reactions and in maintaining constant conditions, the partial pressures and concentrations of the reagents being varied, i.e., in maintaining the $[\text{CuCl}]_{\Sigma}:[\text{Cu}^+]$ and $[\text{Cl}^-]_{\Sigma}:[\text{Cl}^-]$ ratios and, consequently, $[(\text{Cu}_m\text{Cl}_n)^{(n-m)-}]$. In other words, it is necessary to add the initial catalyst (CuCl and, if required, MCl) as the catalyst is trapped by the reagent. The values, which are directly proportional to the activities (and concentrations) of the Cu^+ , Cl^- and H_3O^+ ions (see Section II), can be determined by the potentiometric method (under the conditions of constant cationic content).^{22, 30, 118}

Table 11. Catalytic reactions in the CuCl – NH_4Cl – H_2O system.

Catalytic reaction	Catalytic system	$[\text{CuCl}]$ ($\tilde{m}$)	Ref.
$\text{C}_2\text{H}_2 + \text{HCl} \longrightarrow \text{CH}_2=\text{CHCl}$ (1)	<i>a</i>	5–12	119
$\text{C}_3\text{H}_4 + \text{HCl} \longrightarrow \text{MeC}(\text{Cl})=\text{CH}_2$ (2)	<i>b</i>	0.6–12	120
$\text{C}_3\text{H}_4 + \text{HCl} \longrightarrow \text{MeCH}=\text{CHCl}$ (3)	<i>c</i>	4–12	120
$\text{C}_4\text{H}_4 + \text{HCl} \longrightarrow \text{CH}_2=\text{CHC}(\text{Cl})=\text{CH}_2$ (4)	<i>d</i>	0.5–8	121
$\text{C}_2\text{H}_2 + \text{H}_2\text{O} \longrightarrow \text{MeCHO}$ (5)	<i>e</i>	5–12	119
	<i>f</i> ^a	5–12	122
$\text{C}_3\text{H}_4 + \text{H}_2\text{O} \longrightarrow \text{Me}_2\text{CO}$ (6)	<i>g</i>	0–12	120
	<i>h</i> ^b	4–12	123
$\text{C}_3\text{H}_4 + \text{H}_2\text{O} \longrightarrow \text{MeCH}_2\text{CHO}$ (7)	<i>i</i> ^b	4–12	123
$2\text{C}_2\text{H}_2 \longrightarrow \text{HC}\equiv\text{CCH}=\text{CH}_2$ (8)	<i>j</i>	5–12	95
$3\text{C}_2\text{H}_2 \longrightarrow \text{CH}_2=\text{CHC}\equiv\text{CCH}=\text{CH}_2$ (9)	<i>k</i>	5–12	124
$3\text{C}_2\text{H}_2 \longrightarrow \text{CH}_2=\text{CHCH}=\text{CHC}\equiv\text{CH}$ (10)	<i>l</i>	5–12	125
$\text{C}_2\text{H}_2 + \text{HCN} \longrightarrow \text{CH}_2=\text{CHCN}$ (11)	<i>m</i>	5–10	126
$\text{C}_2\text{H}_2 + \text{cyclopentadiene} \longrightarrow \text{bicyclo[2.2.0]hex-5-ene}$ (12)	<i>n</i>	7–12	13
	<i>o</i>	7–21	13

Note. In the reactions (1–11) $[\text{NH}_4\text{Cl}] = 12 \tilde{m}$; in the reaction (12) $[\text{NH}_4\text{Cl}] = 21 \tilde{m}$. ^a In addition to NH_4Cl , $\text{Cu}_2\text{S}_{\text{solid}}$ is present; ^b in addition to NH_4Cl , RSH is present.

This procedure was used for studying 12 reactions of acetylenic compounds in 15 catalytic systems (Table 11). The kinetic equations obtained under conditions of the constant content of NH_4^+ and at the constant a_{Cu^+} and a_{Cl^-} values are given in Table 12. It was found that the type of equation is independent of the concentration of CuCl (in the kinetic equations, only the observed k_{ij} values are a function of this concentration, where i is the number of the reaction and j is the catalytic system) (see Table 12). In essence, k_{ij} is the function of the stationary concentrations of the $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ complexes and Cl^- ions or of the stationary activities of Cu^+ and Cl^-

$$k_{ij} = f(a_{\text{Cu}^+}, a_{\text{Cl}^-}).$$

In the simplest case (the compositions of the initial copper(I) complex and the intermediate of the first irreversible stage are identical in the Cl^- component), the equation is as follows:

$$k_{ij} = \sum_m \sum_n k_{\text{eff}(m,n)} [(\text{Cu}_m\text{Cl}_n)^{(m-n)-}]. \quad (1)$$

Table 12. Kinetic equations for the reactions of acetylenic compounds in the CuCl – NH_4Cl – H_2O system.

Kinetic equation	Ref.
$r_{1a} = k_{1a} p_{\text{C}_2\text{H}_2} [\text{HCl}]$	119
$r_{2b} = k_{2b} p_{\text{C}_3\text{H}_4} [\text{HCl}] + k p_{\text{C}_3\text{H}_4} a_{\text{Cl}^-}$	120
$r_{3c} = k_{3c} p_{\text{C}_3\text{H}_4} [\text{HCl}]$	120
$r_{4d} = k_{4d} p_{\text{C}_4\text{H}_4} [\text{HCl}] + k p_{\text{C}_4\text{H}_4} [\text{HCl}] (a_{\text{Cl}^-}^2 / a_{\text{H}_2\text{O}})$	121
$r_{5e} = k_{5e} p_{\text{C}_2\text{H}_2} [\text{H}_3\text{O}^+] / (1 + k [\text{H}_3\text{O}^+])$	119
$r_{5f} = k_{5f} p_{\text{C}_2\text{H}_2} [\text{H}_3\text{O}^+] + k p_{\text{C}_2\text{H}_2}$	122
$r_{6g} = k_{6g} p_{\text{C}_3\text{H}_4}$	120
$r_{6h} = k_{6h} p_{\text{C}_3\text{H}_4}$	123
$r_{7i} = k_{7i} p_{\text{C}_3\text{H}_4}$	123
$r_{8j} = k_{8j} p_{\text{C}_2\text{H}_2}^2 / (k p_{\text{C}_2\text{H}_2} + [\text{H}_3\text{O}^+])$	95
$r_{9k} = k_{9k} p_{\text{C}_2\text{H}_2} p_{\text{C}_4\text{H}_4} / (k p_{\text{C}_2\text{H}_2} + [\text{H}_3\text{O}^+])$	124
$r_{10l} = k_{10l} p_{\text{C}_2\text{H}_2} [\text{H}_3\text{O}^+] / (k p_{\text{C}_2\text{H}_2} + [\text{H}_3\text{O}^+])$	125
$r_{11m} = k_{11m} p_{\text{C}_2\text{H}_2} p_{\text{HCN}} / [\text{H}_3\text{O}^+]$	126
$r_{12n(o)} = k_{12n(o)} p_{\text{C}_2\text{H}_2} p_{\text{C}_5\text{H}_6} / [\text{H}_3\text{O}^+]$	13

Note. The subscript in the kinetic equation denotes the number of the reaction and the letter denotes the catalytic system (see Table 11).

The $k_{\text{eff}(m,n)}$ values can be determined only if all complexes present in the system are taken into account, *i.e.*, by solving the system of equations of the same type (1). However, taking into account the presence of a large number of complexes in solution, the large error in the determination of k_{ij} (10%–15%) and the errors in the determination of the total set of complexes, one cannot expect that the coefficients of this system thus obtained reflect the true contributions of individual complexes to the reaction rate. In this connection, the average composition of the complexes, which make the major contribution to k_{ij} both due to the large $k_{\text{eff}(m,n)}$ values and the high concentrations of $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$, was estimated. From Eqn (1) it follows:

$$k_{ij} = \sum_m \sum_n k_{\text{eff}(m,n)} \beta_{m,n} a_{\text{Cu}^+}^m a_{\text{Cl}^-}^n = \sum_m \sum_n k_{m,n} a_{\text{Cu}^+}^m a_{\text{Cl}^-}^n. \quad (2)$$

The a_{Cl^-} value decreases as $[\text{CuCl}]_\Sigma$ increases, because a_{Cu^+} and a_{Cl^-} are interdependent:

$$[\text{CuCl}]_\Sigma = \sum_m \sum_n m \beta_{m,n} a_{\text{Cu}^+}^m a_{\text{Cl}^-}^n, \\ [\text{Cl}^-]_\Sigma = [\text{Cl}^-] + \sum_m \sum_n n \beta_{m,n} a_{\text{Cu}^+}^m a_{\text{Cl}^-}^n,$$

due to which the independent determination of m and n is impossible. It was demonstrated^{126,127} that the a_{Cu^+} and a_{Cl^-} values determined by the potentiometric method are related to each other by the empirical dependence throughout the a_{Cu^+} range met in the systems under consideration ($a_{\text{Cu}^+} = 10^{-8} - 10^{-6}$):

$$a_{\text{Cl}^-} = \frac{a_{\text{Cl}^-}^0}{b a_{\text{Cu}^+}^g}. \quad (3)$$

The b and g coefficients were determined experimentally for each case represented in Table 12. From Eqns (2) and (3) it can be shown that

$$k_{ij} = \sum_m \sum_n k_{m,n} a_{\text{Cu}^+}^m a_{\text{Cl}^-}^n = \sum_m \sum_n \frac{k_{m,n} (a_{\text{Cl}^-}^0)^n}{b^n} a_{\text{Cu}^+}^{m-ng} = \\ = \sum_k k_k a_{\text{Cu}^+}^{l_k}. \quad (4)$$

The average observed order ($\hat{l}$) with respect to a_{Cu^+} can be determined by approximating Eqn (4) by Eqn (5)

$$k_{ij} = k_{\text{eff}(i,j)} \hat{a}_{\text{Cu}^+}^{\hat{l}}, \quad (5)$$

where $\hat{l} = \hat{m} - \hat{n}g$ is the weighted-mean value, which accounts for the l_k values for each complex and the fraction of the reaction rate (θ_k) determined by the participation of the k th complex

$$\frac{d \ln k_{ij}}{d \ln a_{\text{Cu}^+}} = \hat{l} = \sum_k l_k \theta_k. \quad (6)$$

From Eqn (6) it follows that the $\hat{n}$ and $\hat{m}$ values are also weighted-mean. In the general case, the $\hat{l}$ value should be variable, because θ_k can change as the $[\text{CuCl}]_\Sigma$ changes. The fact that the $\hat{l}$ value for all processes is constant throughout the range of CuCl concentrations under study indicates that the $m(n)$ values for the complexes, which make the major contribution to k_{ij} , are similar. To estimate the m and n values and the compositions of the initial $(\text{Cu}_m\text{Cl}_y)^{(y-m)-}$ complexes ($y \neq n$ upon elimination or addition of Cl^- ions in the individual stages of the reaction), the following equation was used:

$$\hat{m} = \frac{\hat{l}}{1-g} + \frac{\hat{q}g}{1-g} = \hat{m}_{\min} + \frac{\hat{q}g}{1-g}, \quad (7)$$

where $\hat{q} = \hat{n} - \hat{m}$.

It was assumed that multiply-charged complexes, which are formed in insignificant amounts in concentrated CuCl solutions,^{22,30,31,33} are not involved in the reactions with acetylenic compounds, and hence analysis of the compositions of the $(\text{Cu}_m\text{Cl}_y)^{(y-m)-}$ complexes was restricted to $y-m = 1$ or 2. In addition, it was assumed that acetylene replaces the water molecule upon the formation of a π -complex, thus retaining the charge of the complex. Then the parameter $\hat{q}$ in Eqn (7) can take the values 0, 1, 2 and 3 depending on the presence of stages of elimination of one Cl^- ion ($y = n + 1$, $\hat{q} = 0$ or 1) and stages of conversion of intermediates with the participation of one Cl^- ion ($y = n - 1$, $\hat{q} = 2$ or 3) as well as on the presence of mechanisms in which $y = n$ ($\hat{q} = 1$ or 2). In this case, the $\hat{m}$ values change from $\hat{m}_{\min}$ ($\hat{q} = 0$) to $\hat{m}_{\min} + 3g/(1-g)$. On these assumptions, $\hat{m} \geq 1$ and $\hat{n} \geq \hat{m}$ have a physical meaning.

The dependence of k_{ij} on $[\text{CuCl}]_\Sigma$ is shown in Fig. 26. Although the k_{ij} value increases as $[\text{CuCl}]_\Sigma$ increases in all cases, the character of $k_{ij} = f([\text{CuCl}]_\Sigma)$ is substantially different for different reactions (see Table 11). For dimerisation (8) of acetylene, hydrocyanation (11) of acetylene, hydration of methylacetylene (6*h* and 7*i*) and acetylene (5*f*) and the reactions with cyclopentadiene (12), the k_{ij} value sharply increases only at $[\text{CuCl}]_\Sigma \geq 5 \hat{m}$, *i.e.*, in the concentration range in which polynuclear complexes (Cu_3Cl_4^- , $\text{Cu}_3\text{Cl}_5^{2-}$, Cu_4Cl_5^- , $\text{Cu}_4\text{Cl}_6^{2-}$, *etc.*) appear in noticeable amounts. The observed order with respect to $[\text{CuCl}]_\Sigma$ is smaller than unity only for the reaction with HCl (4*d*). The observed orders with respect to a_{Cu^+} ($\hat{l}$) are given in Table 13.

The $(\text{Cu}_m\text{Cl}_n\text{CN})^{(n-m+1)-}$ and $[\text{Cu}_m\text{Cl}_n(\text{C} \equiv \text{CH})]^{(n-m+1)-}$ complexes are involved in hydrocyanation (11) and diene condensation (12) of acetylene possessing rate-determining stages. These complexes are formed due to the replacement of the Cl^- ion.

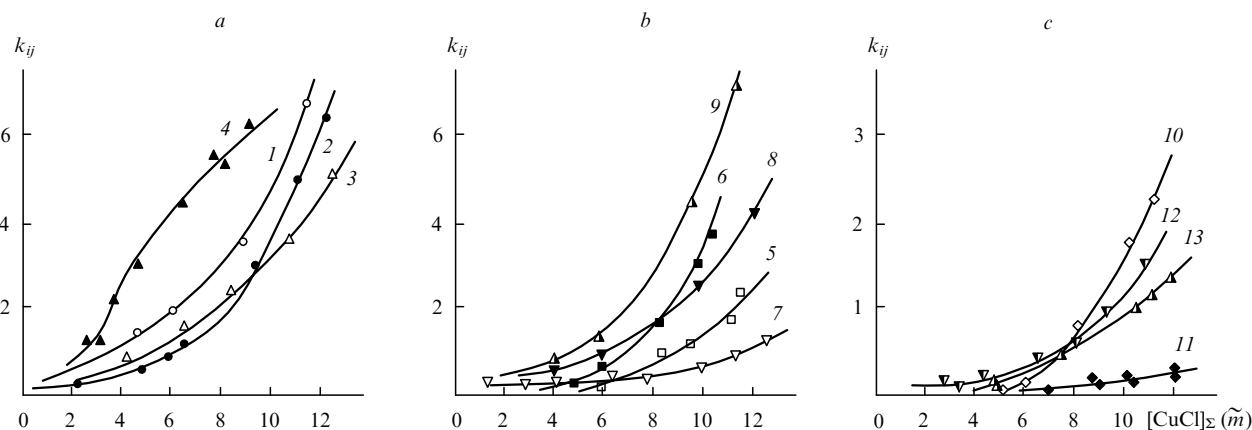
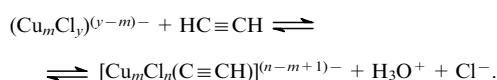


Figure 26. Dependence of k_{ij} on the concentration of CuCl : (1) $k_{1a} \times 10^3$; (2) $k_{2b} \times 10^5$; (3) $k_{3c} \times 10^7$; (4) $k_{4d} \times 0.5 \times 10^5$; (5) $k_{5e} \times 10^3$; (6) $k_{5f} \times 10^2$; (7) k_{6g} ; (8) $k_{6h} \times 0.5 \times 10^5$; (9) $k_{7i} \times 0.5 \times 10^5$; (10) $k_{8j} \times 10^4$; (11) $k_{9k} \times 10^7$; (12) k_{11m} ; (13) $k_{12n} \times 10^6$.

Table 13. The $\hat{m}$ values and the probable compositions of the initial $(\text{Cu}_m\text{Cl}_y)^{(y-m)-}$ complexes.

k_{ij}	$\hat{l}$	g	$\hat{m}_{\min}$ ($\hat{q} = 0$)	$\hat{m}$ ($\hat{q} = 1$)	$(\text{Cu}_m\text{Cl}_y)^{(y-m)-}$ ($\hat{q} = 1$)	$\hat{m}$ ($\hat{q} = 2$)	$(\text{Cu}_m\text{Cl}_y)^{(y-m)-}$ ($\hat{q} = 2$)	$\hat{m}$ ($\hat{q} = 3$)
k_{1a}	0.73	0.29	1.03			1.85	$\text{CuCl}_2^-, \text{Cu}_2\text{Cl}_3^-$	2.25
k_{2b}	0.88	0.33	1.31			2.30	$\text{Cu}_2\text{Cl}_3^-, \text{Cu}_3\text{Cl}_4^-$	2.79
k_{3c}	1.10	0.33	1.64			2.65	$\text{Cu}_2\text{Cl}_3^-, \text{Cu}_3\text{Cl}_4^-$	3.12
k_{4d}	0.71	0.33	1.06			2.26	$\text{Cu}_2\text{Cl}_3^-, \text{Cu}_3\text{Cl}_4^-$	2.54
k_{5e}	0.63	0.32	—	1.49	$\text{CuCl}_2^-, \text{Cu}_2\text{Cl}_3^-$	1.96	$\text{Cu}_2\text{Cl}_4^{2-}$	
k_{5f}	1.16	0.29	1.64	2.04	Cu_2Cl_3^-	2.45	$\text{Cu}_2\text{Cl}_4^{2-}, \text{Cu}_3\text{Cl}_5^{2-}$	
k_{6g}	0.67	0.33	1.00	1.49	$\text{CuCl}_2^-, \text{Cu}_2\text{Cl}_3^-$	1.99	$\text{Cu}_2\text{Cl}_4^{2-}$	
k_{6h}	0.77	0.47	1.45	2.34	$\text{Cu}_2\text{Cl}_3^-, \text{Cu}_3\text{Cl}_4^-$	3.23	$\text{Cu}_3\text{Cl}_5^{2-}, \text{Cu}_4\text{Cl}_6^{2-}$	
k_{7i}	0.99	0.47	1.87	2.75	$\text{Cu}_2\text{Cl}_3^-, \text{Cu}_3\text{Cl}_4^-$	3.64	$\text{Cu}_3\text{Cl}_5^{2-}, \text{Cu}_4\text{Cl}_6^{2-}$	
k_{8j}	2.60	0.32	3.83	4.30	$\text{Cu}_4\text{Cl}_5^-, \text{Cu}_5\text{Cl}_6^-$	4.76	$\text{Cu}_4\text{Cl}_6^{2-}, \text{Cu}_5\text{Cl}_7^{2-}$	
k_{9k}	0.13	0.33	—	—	—	1.18	$\text{CuCl}_3^{2-}, \text{Cu}_2\text{Cl}_4^{2-}$	
k_{10l}	0.64	0.33	—	1.45	$\text{Cu}_2\text{Cl}_3^-, \text{CuCl}_2^-$	1.94	$\text{Cu}_2\text{Cl}_4^{2-}$	
k_{11m}	2.21	0.39	3.62	4.26	$\text{Cu}_4\text{Cl}_6^{2-}, \text{Cu}_5\text{Cl}_7^{2-}$			
k_{12n}	1.52	0.60	3.80	5.30	$\text{Cu}_5\text{Cl}_7^{2-}, \text{Cu}_6\text{Cl}_8^{2-}$			
k_{12o}	2.02	0.60	5.05	6.55	$\text{Cu}_7\text{Cl}_9^{2-}$			

Note. At $\hat{q} = 0$, the $(\text{Cu}_m\text{Cl}_y)^{-}$ complexes with $m = 3$ and 4 (catalytic systems m and n) and $m = 5$ (catalytic system o) are involved in the reactions (11) and (12), respectively.



Hence, $y = n + 1$ (at $\hat{q} = 0$ or 1) and $\hat{m}_{\min} = 3.6 - 5.0$ for the reactions (11) and (12). In the reactions (8)–(10), which proceed without rate-determining stages, $\hat{q}$ reflects the composition of the transition state ($y = n$). Polynuclear complexes with $m = 3 - 7$ are involved in the reactions (8), (9) and (12) (see Table 3).

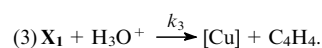
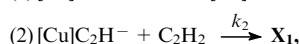
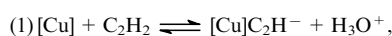
The participation of polynuclear Cu(I) complexes in the dimerisation of acetylene (8) was confirmed by spectrophotometric studies of the dependence of the dimerisation rate on the concentration of the ‘yellow’ complexes $[\text{Cu}_4\text{Cl}_4(\text{C}\equiv\text{CH})^-]$ and $[\text{Cu}_4\text{Cl}_5(\text{C}\equiv\text{CH})^{2-}]$ and on their compositions as a function of a_{Cu^+} , a_{Cl^-} , $p_{\text{C}_2\text{H}_2}$ and $[\text{H}_3\text{O}^+]$ ⁵⁸ (see Section III) and was additionally supported by isolation of crystalline copper chloride and ethynyl complexes formed in the catalytic Nieuwland system (the structures of these complexes are considered in Sections II and III).

2. Kinetics and crystal-chemical aspects of the mechanism of Nieuwland oligomerisation of acetylene

Comprehensive investigations of the kinetics of dimerisation^{58, 95, 125, 128–131} and trimerisation^{124, 125} of acetylene made it possible to state the major features of the mechanism of these reactions. Let us consider dimerisation of acetylene (8) (see Table 11) giving rise to vinylacetylene (VA) in detail. At constant activities of Cu^+ and Cl^- , i.e., at constant concentrations of catalytically active complexes, the reaction rate r_{VA} is described by the equation

$$r_{\text{VA}} = \frac{k_{\text{H}} p_{\text{C}_2\text{H}_2}^2}{k p_{\text{C}_2\text{H}_2} + [\text{H}_3\text{O}^+]}. \quad (8)$$

A two-stage mechanism without a rate-determining stage corresponds to this equation, where the copper chloride complex is denoted by $[\text{Cu}]$

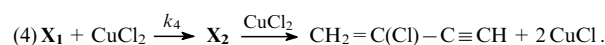


The stages 1 and 2, which follow unambiguously from the kinetics, are supplemented by the stage 3, which is required to obtain the final stoichiometric equation for the catalytic reaction (8). It was also found that the k constant in the denominator is independent of $[\text{CuCl}]_{\Sigma}$ (and a_{Cu^+}), but depends on a_{Cl^-} ($k = k'/a_{\text{Cl}^-}$). This fact leads to the equation

$$r_{\text{VA}} = \frac{k'_{\text{H}} p_{\text{C}_2\text{H}_2}}{k' p_{\text{C}_2\text{H}_2} + [\text{H}_3\text{O}^+][\text{Cl}^-]}, \quad (9)$$

according to which Cl^- and H_3O^+ are eliminated in the same stage (the stage 1 or the following quasi-equilibrium stage).

Data on the composition of the intermediate X_1 (and to some extent on its nature) were obtained in studies of the kinetics of the preparation of vinylacetylene and 2-chlorovinylacetylene (CVA) in systems containing additionally small concentrations ($\sim 10^{-3}$ mol litre⁻¹) of CuCl_2 .^{132, 133} In the presence of CuCl_2 , the conversion of the intermediate X_1 takes two competitive paths, viz., the stages 3 and 4



Under these conditions, the sum of the rates r_{VA}^* and r_{CVA} is equal to the rate of formation of X_1 (i.e., r_{VA}). The rate ratio is described by the equation

$$\frac{r_{\text{VA}}^*}{r_{\text{CVA}}} = \bar{K} \frac{[\text{H}_3\text{O}^+]}{[\text{CuCl}_2]}, \quad (10)$$

where $\bar{K} = k_3/k_4$.

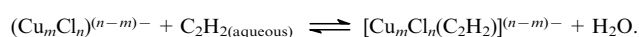
As a result, the equation for the rate of formation of vinylacetylene includes the concentration of the H_3O^+ ion, which is involved in the stage 3 after the irreversible stage 2

$$r_{\text{VA}}^* = \frac{k_{\text{H}} p_{\text{C}_2\text{H}_2}^2}{k p_{\text{C}_2\text{H}_2} + [\text{H}_3\text{O}^+]} \cdot \frac{\bar{K}[\text{H}_3\text{O}^+]}{\bar{K}[\text{H}_3\text{O}^+] + [\text{CuCl}_2]}. \quad (11)$$

As a consequence, the rate of formation of vinylacetylene (r_{VA}^*) passes through a maximum as $[\text{H}_3\text{O}^+]$ changes. It was

suggested that the intermediate **X₁** with composition [Cu]₄H₃ was formed due to the insertion of acetylene at the Cu–C≡CH bond, *i.e.*, this intermediate is the β-ethynylvinyl derivative of copper (CuCH=CHC≡CH). The reaction of **X₁** (successively with two CuCl₂ molecules) afforded only chlorovinylacetylene. An analogous process took place in the reaction of CuCH=CHCl with two CuCl₂ molecules to form CH₂=CCl₂ (acidolysis yielding CH₂=CHCl was the competitive process).^{134, 135} The formation of chlorovinylacetylene from the intermediate **X₁** (it is the intermediate common to vinyl- and chlorovinylacetylenes) is also confirmed by the fact that none of such compounds as vinylacetylene, diacetylene, vinylidene chloride or vinyl chloride in these systems is converted into chlorovinylacetylene under the above-mentioned conditions.^{132, 133} Investigation of the effect of the addition of HgCl₂ on the synthesis of vinylacetylene demonstrated¹³¹ that an increase in the acidity of the CuCl–NH₄Cl–H₂O systems upon the addition of HgCl₂ is associated with an exchange reaction giving rise to the organomercury derivative ClHgCH=CHC≡CH, which is stable to HCl. Vinylacetylene can be isolated from this derivative only under the action of concentrated HCl.

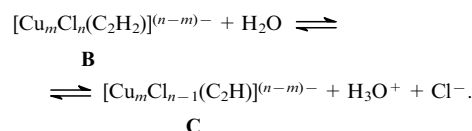
Let us consider the stages 1–3 in more detail. Activation of acetylene resulting in its deprotonation (stage 1) occurs, most likely, in the course of several reactions the first of which involves the formation of π-complexes **B**

**A****B**

Kinetic studies demonstrated that replacement of Cl[–] in this stage is contradictory to Eqn (9). The formation of the π-complex can occur either in the course of the replacement of the coordinated water molecule or as a result of the cleavage of the μ–Cl bond without the replacement of Cl[–]. The replacement of the bridging chlorine atom accompanied by its migration to other coordination vacancies can also occur. Based on the assumption that the short-range order of complexes dissolved in concentrated solutions (which is similar to that in a melt), for example, of Cu₃Cl₅^{2–} (see Refs 48 and 49), corresponds to the structure of the complex **9a** in the crystalline state (*T*_{m.p.} ≈ 80 °C), the process of replacement of the water molecules can be represented by the scheme shown in Fig. 27. In this process, the formation of the intermediate **B** is accompanied by the migration of the bridging chlorine atom in the complex **A** to the coordination site, which was previously occu-

ried by the water molecule of crystallisation (this molecule is hatched in Fig. 27). The intermediate **B** (more precisely, the coordination π-unit) is structurally similar to one of the π-complexes (**20**, **21a,b**, **22** or **23**).

The reaction of the π-complex (**B**) with a water molecule affords the acetylenide (ethynyl) intermediate **C**. In this case, the Cl[–] ion can be eliminated simultaneously with H₃O⁺, but it can also be eliminated in the following quasi-equilibrium stage, the type of the kinetic equation being the same



Among a wide diversity of the structures of ethynyl compounds (see Section III), the complexes **43** and **44** (see Fig. 13) correspond to the intermediate **C** whose existence was suggested in the study⁹⁶ without convincing reasons.

As mentioned above, variations in the partial pressure of acetylene (*p*_{C₂H₂}) and [H₃O⁺] with the maintenance of constant *a*_{Cu+} and *a*_{Cl–}, *i.e.*, the concentrations of the active copper chloride complex, allows one to solve the question as to what particular σ-organometallic compound, which is present in the solution, serves as an intermediate in the catalytic reaction. In the synthesis of vinylacetylene, an unsymmetrical ethynyl complex serves as such an intermediate. In solution, other ‘yellow’ complexes, for example, the symmetrical acetylenide complex [(Cu₂C₂)(Cu_pCl_q)]^{(q–p)–} existing in equilibrium with the [(Cu_mCl_{n–1})(C₂H)]^{(n–m)–} ion, are present in solution depending on pH. The above-mentioned inactive complex enters into the material balance with respect to [CuCl]_Σ. Hence, the reaction rate of the formation of vinylacetylene passes through a maximum as the concentration of HCl changes if the concentration of (Cu_mCl_n)^{(n–m)–} is not maintained constant.¹²⁸ The maximum rate is observed in the range pH = 1.5–0.9 ([HCl] = 0.05–0.15 *m*). In this case, an increase in the acidity of the solution (pH < 1.5) leads to destruction of symmetrical acetylenide and to an increase in the concentration of unsymmetrical [Cu]C₂H acetylenide. A further increase in the acidity leads to the disappearance of this intermediate and to a decrease in the rate to zero. The formation of a complex containing the Cu₂C₂ fragment of the type **45** at pH = 4 and low temperature is in complete agreement with the above reasoning and observations.

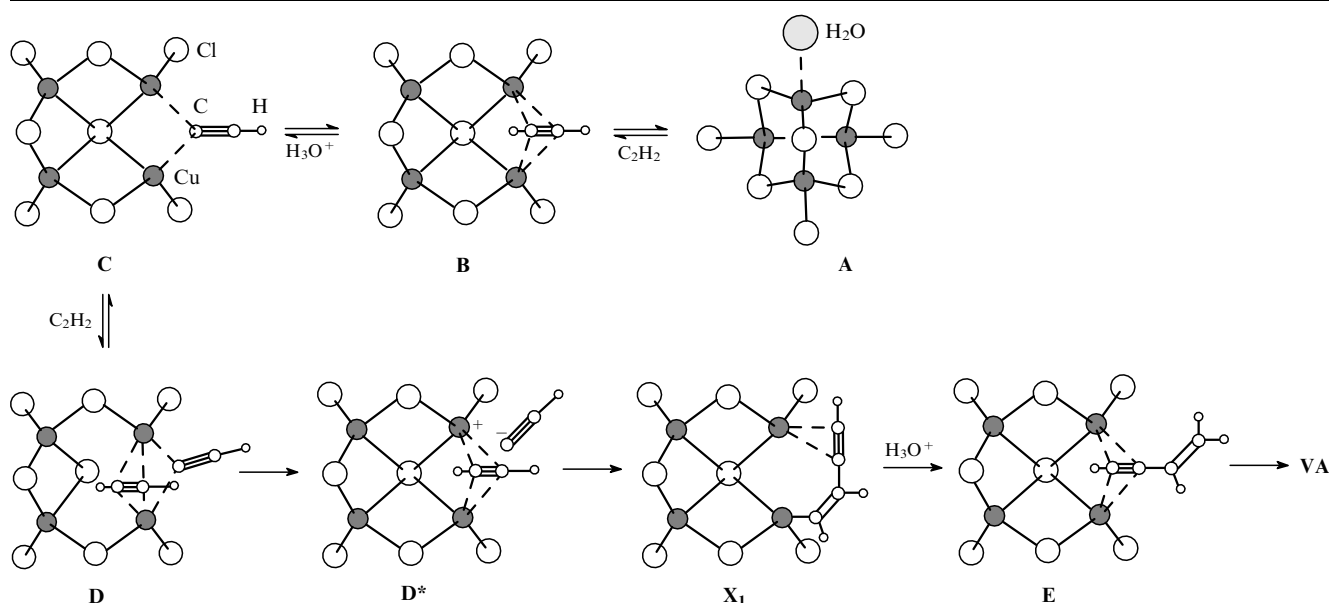
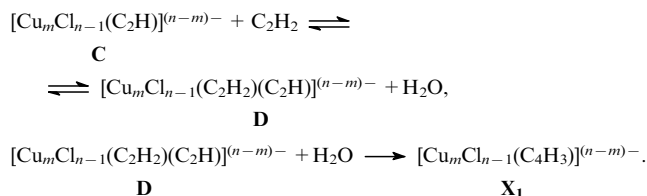
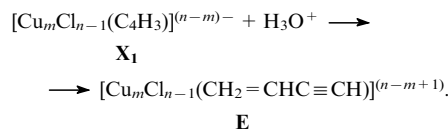


Figure 27. Structural changes in the course of catalytic oligomerisation of acetylene.

Evidently, the subsequent stage of the Nieuwland process (stage 2) giving rise to the intermediate **X₁** involves the insertion of acetylene at the Cu–C₂H bond to form the CuCH=CHC≡CH fragment whose acidolysis affords C₄H₄. Below are represented the stages of the conversion of the intermediate **C** into the intermediate **X₁** (see Fig. 27).

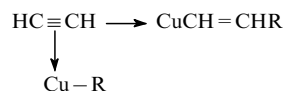


The stage of acidolysis of the intermediate **X₁** (the electrophilic replacement of the Cu atom by the H⁺ ion in the Cu–CH= fragment) is beyond question. This stage was confirmed by the kinetic data [Eqn (11)]. The reaction proceeds very readily even with water.^{136, 137} Stages of this type were also observed in hydration, hydrochlorination and hydrocyanation of acetylene.¹³



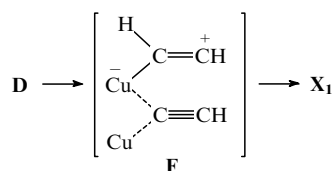
The intermediate **E** decomposes to form vinylacetylene (it can be replaced by acetylene) or is involved in trimerisation of acetylene to give hexa-1,5-dien-3-yne [divinylacetylene (DVA)].

The insertion of acetylene giving rise to the intermediate **X₁** is the most important and intricate stage of the process. The fact of insertion is beyond a doubt because the reactions of cuprates R₂Cu·MgX and RCu·MgX₂ with alkynes are well known^{136, 137} and proceed stereoselectively (100% *syn*-addition) under mild conditions. However, the question about the mechanism of the process of insertion remains open. In the mononuclear case, the stage of insertion

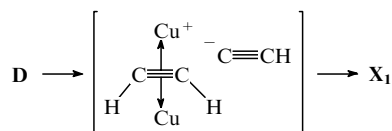


is not an elementary concerted process because it is symmetry-forbidden due to the *d*¹⁰ configuration and *sp*³ hybridisation of the atomic orbitals of Cu(I).¹³⁸ Three alternative paths are formally possible.

1. The formation of the metallocarbenium ion (**F**) followed by the rapid migration of the ethynyl group giving rise to the intermediate **X₁** in the first irreversible stage.

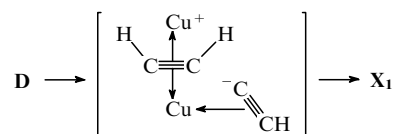


2. Dissociation of the [Cu](μ-η¹-C≡C) bond to form the contact ionic pair followed by the addition of the carbanion to the η²-coordinated acetylene.



3. Dissociation of the bridging [Cu](μ-η¹-C≡C) bond accompanied by the conversion of the ethynyl group into the η²-state

followed by the addition of the η²-HC≡C[−] carbanion to η²-alkyne.



Path 1 was considered¹³ for the reactions of cationic Pt(II) complexes with alkynes. This path was assumed¹³ for reactions with the participation of Hg²⁺, but it is less probable for Cu(I) halides. Path 3 is more interesting because a softer nucleophile and a weak base (η²-HC≡C[−]) are involved in the reaction. In addition, paths 2 and 3 provide a more adequate explanation for the high stereoselectivity of the insertion of alkynes. To discuss these alternatives, let us use the data on the structures of the complexes (PyH)₄Cu₉Cl₁₂(C≡CH) (**44**) and NH₄Cu₈.Cl₉(HC≡CH)₄·2/5{[Cu(H₂O)₂]·[CuCl₂]·H₂O} (**23**). Crystal-chemical analysis demonstrated that these compounds are genetically related (Fig. 28). The subunit Cu₈Cl₉ (Fig. 28 *b*) is common to both complexes. This subunit contains four pairs of [Cu₂] ‘matrices’ with the Cu···Cu distance of ~2.8 Å. The η²,η²-coordination of one C₂H₂ molecule at the [Cu₂] matrix each affords the structural fragment shown in Fig. 28 *c*. The coordination of the η¹,η¹-C≡CH ligand at the [Cu₂] matrix gives rise to the fragment shown in Fig. 28 *a*. The relation between the fragments (*a*) and (*c*) suggests the possible stereochemistry of the second and third paths of conversions of the intermediate **D** into **X₁**. Probably, the intermediate **D** is formed by the replacement of the σ-coordinated μ₄-Cl ligand in the complex with acetylene (μ-η²,η²-C₂H₂). The resulting complex **D** (see Fig. 27) contains simultaneously several ligands coordinated at the [Cu₂] matrix, *viz.*, η¹,η¹-C≡CH and η²,η²-C₂H₂. The intermediate **D** can be converted into **X₁** *via* two paths. From the viewpoint of the stereochemistry, the path 2 is the most favourable and involves the cleavage of the Cu–C η¹-bond to form the contact ionic pair **D*** (see Fig. 27). The [−]C₂H ion rapidly attacks one of the C^{δ+} atoms of the π-bonded C₂H₂ molecule. In the case of the path 3, the η¹,η¹-C≡CH ligand should be converted into the η¹,η²-C≡CH ligand. Then the Cu–C η¹-bond can be cleaved followed by the attack of the η²-coordinated anion on the η²-acetylene. Protolysis of the intermediate **X₁** affords π-coordinated vinylacetylene (Fig. 27, the intermediate **E**).

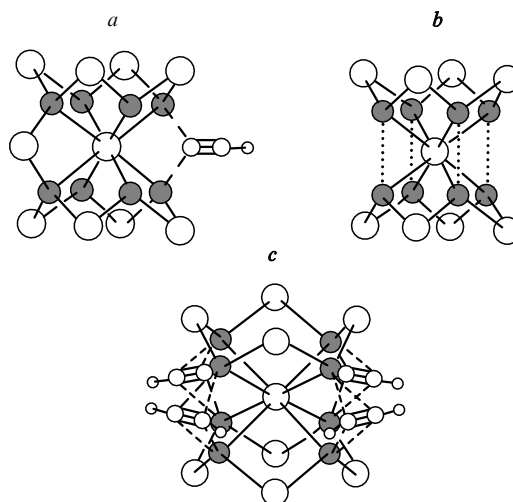
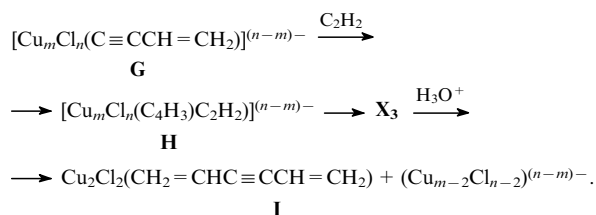


Figure 28. Structural fragment of the (PyH)₄Cu₉Cl₁₂(C≡CH) complex (**44**) (*a*), the Cu₈Cl₉ subunit (*b*) and the structural fragment of the NH₄Cu₈Cl₉(HC≡CH)₄·2/5{[Cu(H₂O)₂]·[CuCl₂]·H₂O} complex (**23**) (*c*).

The $[\text{Cu}_m\text{Cl}_n(\text{C}_4\text{H}_4)]^{(n-m)-}$ complex (**E**) can be deprotonated to form the intermediate **G** (of the type **55**, see Fig. 22). Judging from the kinetic data, the latter is converted into divinylacetylene.

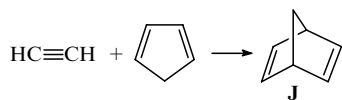


Protolysis of the intermediate X_3 (an analogue of X_1) yields the intermediate **I** (complex **34**).

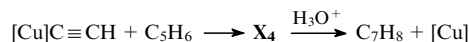
The intermediate X_1 can interact with yet another acetylene molecule (through the π -complex), which can be inserted at the $\text{Cu}-\text{CH}=\text{CH}_2$ bond, because the insertion of alkynes at the $\text{Cu}(\text{I})$ -alkenyl bond occurs rather readily.¹³⁷ As a result, hexa-1,3-dien-5-yne (the isomer of divinylacetylene) is formed. On certain assumptions, the scheme of its formation agrees with the kinetic data.¹³

3. Addition of cyclopentadiene and HCN to acetylene

The Diels–Alder reaction (12) of acetylene with cyclopentadiene to form norbornadiene **J** proceeds efficiently in highly concentrated solutions of CuCl .

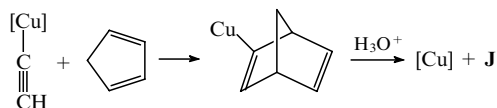


The polynuclear complexes Cu_5 , Cu_6 and Cu_7 also participate in this reaction. The process involves the rate-determining stage because the reaction

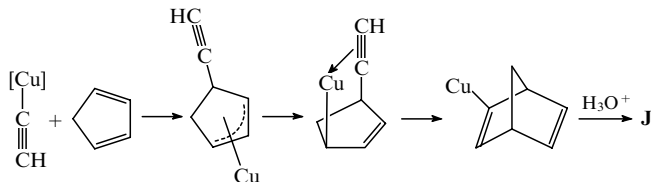


proceeds more slowly than the reaction of the ethynyl intermediate with C_2H_2 . Two possible mechanisms of formation and conversion of X_4 should be considered.

1. The classical diene synthesis, *viz.*, [4 + 2]-cycloaddition, with the participation of an active (polarised) dienophile.



2. The insertion of diene at the $\text{Cu}-\text{C}$ bond to form the η^3 -allylic intermediate followed by the repeated intramolecular insertion of $\text{C}\equiv\text{CH}$ at the $\text{Cu}-\text{C}$ bond.



Hydrocyanation of acetylene (11, see Table 12) to form acrylonitrile proceeded in more acidic solutions of CuCl (the HCl content was up to 3 mass %). The process involves the rate-determining stage. At constant a_{Cu^+} and a_{Cl^-} , the process is described by the equation

$$r_{11m} = \frac{k_{11m} p_{\text{C}_2\text{H}_2} p_{\text{HCN}}}{[\text{H}_3\text{O}^+]}. \quad (12)$$

If the concentrations of the active components are not maintained constant, the reaction rate passes through a maximum both

as p_{HCN} and the concentration of H_3O^+ change.¹²⁶ Although the conclusion about the participation of the free CN^- ion or a complex containing the $\sim\text{CuCN}$ fragment cannot be made because of the presence of the rate-determining stage, the experimental data give grounds to suggest that the mechanism is analogous to that of dimerisation of acetylene. The concentration of free cyanide ions in acidic solutions of CuCl cannot be higher than $10^{-9} - 10^{-10} \text{ mol litre}^{-1}$ due to which the attack of the free cyanide ion present in solution on the π -coordinated acetylene ligand is improbable, as in the case of the $\text{HC}\equiv\text{C}^-$ anion in the dimerisation of acetylene.

Catalysis of hydrocyanation of acetylene in concentrated solutions makes it possible to achieve high concentrations of the copper cyanide complex $\sim\text{CuC}\equiv\text{N}$. Thus the concentration of dissolved CuCN in the $\text{CuCl}-\text{NH}_4\text{Cl}-\text{H}_2\text{O}$ system can reach 15 mass %. If HCN is passed through these systems, different mono- and polycyanide complexes of copper, *viz.*, $[\text{Cu}_m\text{Cl}_{n-1}(\text{CN})]^{(n-m)-}$ and $[\text{Cu}_m\text{Cl}_{n-x}(\text{CN})_x]^{(n-m)-}$, can be formed depending on the concentration of HCl . High reactivities of polynuclear cyanide complexes are also associated with their bridging structures analogous to those of the complex $\text{NH}_4\text{Cu}_2(\text{CN})_3 \cdot \text{H}_2\text{O}$ ¹³⁹ (Fig. 29 *a*) or $\text{KCu}_2(\text{CN})_3 \cdot \text{H}_2\text{O}$.¹⁴⁰ In addition, due to the bridging structure, CN^- can be held as an anion in the coordination sphere of the $(\text{Cu}^+\text{C}^-\equiv\text{NCu})$ complex in the course of insertion of acetylene at the $\text{Cu}-\text{CN}$ bond. Acrylonitrile formed after acidolysis of the intermediate $\text{CuCH}=\text{CHC}\equiv\text{NCu}$ can be coordinated to form the π -complex of the type $2\text{CuCl} \cdot \text{CH}_2=\text{CHCN}$.¹⁴¹ In the latter, the acrylonitrile molecule serves as the bridging η^2 - (at the $\text{C}=\text{C}$ bond) and η^1 - (at the N atom) ligand. Interestingly, the CN^- ion can be replaced in the structure of the cyanide complex $\text{KCu}_2(\text{CN})_3 \cdot \text{H}_2\text{O}$ by the C_2^{2-}

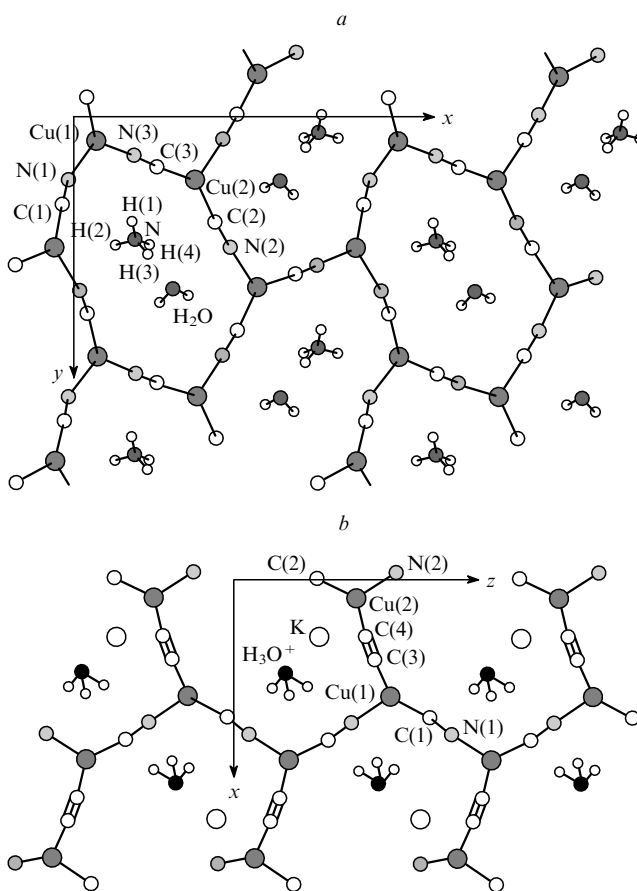
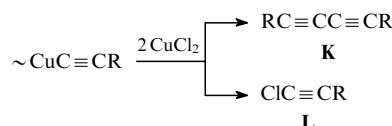


Figure 29. The $[\text{Cu}_2(\text{CN})_3]_n^-$ anions in the structure of the $\text{NH}_4\text{Cu}_2(\text{CN})_3 \cdot \text{H}_2\text{O}$ complex¹³⁹ (*a*) and the $[\text{Cu}_2(\text{CN})_2(\text{C}\equiv\text{C})_2]_n^-$ anions in the structure of the $[\text{K}(\text{H}_3\text{O})^+][\text{Cu}_2(\text{CN})_2(\text{C}\equiv\text{C})_2]$ complex¹⁸ (*b*).

dianion (Fig. 29b) to form the complex $[K(H_3O^+) \cdot [Cu_2(CN)_2(C \equiv C)]]^{18}$

4. Participation of ethynyl copper complexes in homogeneous oxidative conversions of alkynes in the CuCl–MCl–CuCl₂ systems

Many oxidative conversions of acetylene and alkynes proceed in concentrated solutions of CuCl in the presence of CuCl₂.^{13, 142} As mentioned above, 2-chlorobut-1-en-3-yne,^{132, 133} *trans*-1,2-dichloroethylene and 1,1-dichloroethylene^{134, 135} formed from acetylene in these systems. Soluble σ -ethynyl derivatives are also involved in oxidative dehydrocondensation of alkynes yielding substituted diacetylenes **K**^{13, 143} and in substituting oxidative chlorination giving rise to chloroalkynes **L**.^{144–147}



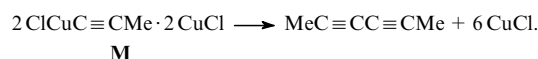
The CuCl–CuCl₂ catalytic systems (CuCl₂ is a catalyst in the presence of O₂ or in an electrochemical system) are characterised by the formation of heterovalent polynuclear complexes very typical of copper.¹⁴⁸ The structure of the simplest representative of these complexes, *viz.*, $[(C_2H_5)_4N]Cu_2Cl_4$, has been described.¹⁵ The Cu(I) and Cu(II) centres in the polynuclear chain $(Cu_2Cl_4)_n^{n-}$ differ in symmetry.

Concentrated solutions, which enable one to achieve high concentrations of intermediates ($\sim CuC \equiv CR$, $\sim CuCN$ or $\sim CuCH=CHX$), play an important role in the catalysis of addition at the $C \equiv C$ bonds of the $HC \equiv CH$, HCl , HOH , HCN and C_5H_6 molecules. In oxidative conversions of alkynes, electron transfer from CuR to $CuCl_2$ in mixed complexes occurs so rapidly ($k = 0.5 \times 10^8 \text{ mol}^{-1} \text{ litre s}^{-1}$)¹⁴⁹ that the reaction rates are high even in solutions dilute with respect to CuCl (for example, at the concentrations of LiCl, CuCl and CuCl₂ equal to 5, 0.2 and 0.5 mol litre⁻¹, respectively). The kinetic equations for some reactions proceeding in these systems under conditions of constant high concentration of the cations (Li^+) {when $[CuCl]_{\Sigma} \propto [(CuCl_n)^{(n-1)-}]$ and $[CuCl_2]_{\Sigma} \propto [(CuCl_n)^{(n-2)-}]$ } were obtained. Thus, the rate of oxidative dimerisation of methylacetylene (MA) is described by the equation¹⁴²

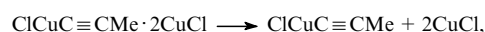
$$r_{DDA} = \frac{k_{DDA} p_{MA} [CuCl_2] [CuCl]^2}{[H_3O^+]}, \quad (13)$$

where DDA is dimethyldiacetylene.

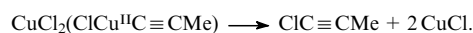
The process occurs through the intermediate $CuC \equiv CMe$ and involves the rate-determining stage whose transition state includes Cu(I) and Cu(II) ions $[2Cu(I) \cdot Cu(II)(-C \equiv CR)]^\ddagger$. It should be noted that two CuCl molecules enter into the reaction even in rather dilute solutions. Apparently, these molecules are required for stabilisation of the assumed intermediate, *viz.*, the ethynyl complex of copper(II) ($ClCuC \equiv CMe$). The kinetic data¹⁴² demonstrate that two molecules of the intermediate decompose to form dialkyne



It may be suggested that the ethynyl group in the **M** complex acts as the μ_3 - η^1, η^2, η^2 -ligand. It is also conceivable that two CuCl molecules act as catalysts in the formation of $ClCu^I C \equiv CMe$



The reaction of $\sim Cu^I C \equiv CMe$ with two CuCl₂ molecules affords 1-chloroprop-1-yne (CP). The latter is formed in two stages the first of which is rate-determining.



The reaction rate is described by the equation

$$r_{CP} = \frac{k_{CP} p_{MA} [CuCl_2]^2 [CuCl]}{[H_3O^+]}. \quad (14)$$

It should be noted that heterovalent copper complexes with organic ligands (of the σ - and π -types) are as yet unknown although the complex **15** may be assigned to heterovalent organo-metallic complexes because its structure contains Cu^{2+} ions occupying octahedral cavities and $CuC \equiv CH$ species as 'guests' along with the 'host' complexes.

V. Conclusion

Analysis of the experimental data obtained in studies of the compositions and structures of the complexes $M_{(n-m)}Cu_mCl_n$ in solutions and in the solid phase, copper(I) π -complexes with acetylene and its derivatives and σ -ethynyl compounds, and information gained from investigations of the kinetics of the catalytic conversions of alkynes in the $MCl-CuCl-H_2O$ and $MCl-CuCl-CuCl_2-H_2O$ systems reveals the specific features of the coordination chemistry of copper(I) halide complexes and the peculiarities of the behaviour of copper(I) as a catalyst of conversions of acetylenic compounds.

The formation of coordination polyhedra through bridging chloride (bromide) ligands in which Cl^- acts as the μ_2 -, μ_3 - or μ_4 -ligand gives rise to low-charged polynuclear associates $(Cu_mCl_n)^{(n-m)-}$, which can efficiently interact with acetylene and alkynes to form various π - and σ -organometallic compounds.

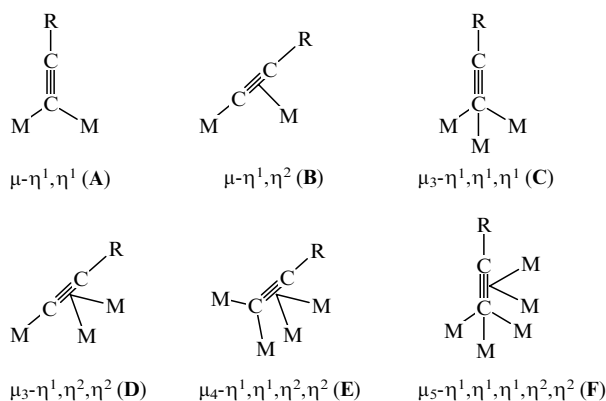
The geometric characteristics of the π -coordination polyhedra about the Cu(I) atoms and of the triple $C \equiv C$ bond π -activated at the metal centre in the CuCl π -complexes with acetylene and its derivatives and the higher efficiency of the Cu(I)–($C \equiv C$) π -interaction compared to that of Cu(I)–($C=C$) are consistent with the statement that two degenerate π -MOs are split into two MOs with different energies ($\pi_{||}$ and $\pi_{\perp}$) in the course of π -bonding with Cu(I) due to which the reactivities of alkynes increase. Using the copper(I) halide π -complexes of organic compounds containing the $C \equiv C$ bond as an example, two qualitatively different modes of π -coordination of the $C \equiv C$ groups to the Cu(I) atoms were revealed. These modes differ in the efficiency of the π -interaction. Thus, the first mode of coordination occurs in the case of the probable simultaneous participation of $\pi_{||}$ -, $\pi_{||}^*$ and $\pi_{\perp}^*$ -MOs to form the Cu(I)–($C \equiv C$) π -unit. The second mode of coordination occurs if two individual π -MOs of the $C \equiv C$ bond interact with the Cu(I) atom independently of one another giving rise to the bridging Cu(I)–($C \equiv C$)–Cu(I) π -unit (η^2, η^2 - $HC \equiv CR$). In the latter case, each π -MO of the acetylene group behaves analogously to that of the ethylene group and is independently coordinated to one metal atom. The participation of the higher $\pi_{||}$ -MO and two π^* -MOs is favourable for an increase in the contribution both of the donor-acceptor and dative components of the bond due to which Cu(I)–alkyne bonding in the first case is more efficient.

In the crystalline anionic π -complexes of CuCl with acetylene and its monosubstituted derivatives, the efficiency of the Cu(I)–($C \equiv C$) π -interaction, which is manifested in the elongation of the π -coordinated $C \equiv C$ bond, is substantially affected by $\equiv C-H \cdots Cl$ hydrogen bonds (the length of the π -coordinated $C \equiv C$ bond depends linearly on the $H \cdots Cl$ distance). The reason is that the Cl atoms whose electron-withdrawing properties depend substantially on the strength of the $M^+ \cdots Cl^-$ ionic interaction can affect the polarisation of the $\equiv C-H$ bond of the π -coordinated molecule of terminal alkyne through the $C(H) \cdots Cl$ contact due to which the electron density on the carbon atoms can increase or decrease resulting in the corresponding decrease or increase of the contribution of the dative transfer

$\text{Cu(I)} \rightarrow (\text{HC} \equiv \text{CR})$. In this case, the $\text{C} \equiv \text{C}$ bond is subjected to an insignificant or substantial elongation, respectively.

The high efficiency of π -interactions in copper(I) complexes of the ethynyl type (σ, π -complexes) whose formation in the $\text{MCl}-\text{CuCl}-\text{H}_2\text{O}$ systems (according to the kinetic data) plays a decisive role in many conversions of C_2H_2 and alkynes is associated with the mutual strengthening of individual types of interactions, viz., of $\text{Cu(I)}-(\eta^1\text{-C} \equiv \text{CR})$ and $\text{Cu(I)}-(\eta^2\text{-C} \equiv \text{CR})$. This effect of mutual strengthening (synergism) of acetylenide and π -types of interactions, which was revealed in cluster acetylenides and ethynyl complexes of Cu(I) , is often accompanied by unusual structural manifestations and by the appearance of qualitatively new properties of the $\text{C} \equiv \text{C}$ group π -activated at the metal centre [the $\text{C} \equiv \text{C}^-$ dianion in the compound **45** can be π -coordinated simultaneously to three Cu(I) atoms].

In addition to the modes of coordination of ethynyl groups ($\text{C} \equiv \text{CR}$) to the copper(I) atom (**A**, **B**, **C** and **D**) known in organometallic chemistry,^{96–117} new types of clusters (**E** and **F**) were found in the case of copper chloride complexes.



The polydentate character of coordination of acetylene in π -complexes and of ethynyl ligands in σ -organometallic compounds (as well as of cyanide groups) is the governing factor responsible for the catalytic activity of polynuclear Cu(I) complexes, which is characterised by the following features.

1. The high rate of cleavage of the bridging $\text{Cu}-\text{Cl}$ ($\mu, \mu_3, \mu_4\text{-Cl}$)-bonds to form the initial π -complexes (in some cases, the $\mu\text{-Cl}$ atom is isolobally replaced by alkyne).

2. The high solubility of such molecules as $\text{Cu} \equiv \text{CH}$, $\text{CuC} \equiv \text{CR}$ and CuCN due to reactions with polynuclear $(\text{Cu}_m\text{Cl}_n)^{(n-m)-}$ anions and, consequently, the high concentration of intermediates in solutions (the concentration of 'yellow' acetylenide complexes in the Nieuwland reaction reaches $0.1 \text{ mol litre}^{-1}$).

3. The bridging nature of the coordinated ethynyl and cyanide groups provides various stereochemical possibilities for the appearance of carbanionic ($\text{RC} \equiv \text{C}^-$) and cyanide ($\text{N} \equiv \text{C}^-$) nucleophiles in the complex.

4. The tendency for cluster-formation in polynuclear σ, π -ethynyl complexes has a particular effect on the course of catalytic processes.

5. All stages of the process, including coordination of the products, can occur on the 'matrix' of one complex formed from the $[\text{Cu}_n]$ cluster.

6. The formation of polynuclear heterovalent complexes in oxidation reactions is favourable for the electron transfer in multiple-electron processes.

7. Hydration and hydrochlorination of alkynes in which the σ -organometallic intermediate is formed in the course of the attack of the nucleophile (Cl^- or H_2O), which is present in the solution of the copper(I) π -complex, can also occur without the participation of polynuclear complexes and, correspondingly, need not be catalysed by concentrated solutions.

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Reactions of nitrogen oxides with polymers[†]

G B Pariiskii, I S Gaponova, E Ya Davydov

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Abstract. The mechanisms of the reactions of nitrogen oxides and different classes of solid polymers are considered. Particular emphasis is given to the analysis of the mechanisms of the formation of stable nitroxyl radicals. Double bonds and amide groups of macromolecules, as well as hydroperoxides and peroxide macroradicals are shown to be involved in the reactions with nitrogen oxides. The application of nitrogen oxides for the preparation of spin-labelled polymers and the use of the ESR imaging technique (ESR tomography) for the investigation of the structure of the reaction front during nitration of solid polymers are considered. The bibliography includes 111 references.

I. Introduction

Investigations aimed at finding relations between the processes of thermal, thermal-oxidative, photolytic, photo-oxidative and mechanochemical ageing of different classes of polymers and destruction effects, as well as studies on stabilisation of polymers to withstand these effects have been carried out for a long time. The main goal of these investigations is to retain the operating characteristics of polymeric materials.

Among numerous publications devoted to generalisation of the results obtained in this area of scientific exploration (see, *e.g.*, Refs 1–20), monographs by Emanuel and Buchachenko^{2,4} can be highlighted. In these studies, the kinetics of the ageing of polymers under the action of different factors have been analysed taking account of specific features of elementary acts of the corresponding solid-phase chemical transformations.

In the mid-twentieth century, it was recognised that the increasing amount of industrial waste discharged to the atmosphere pollutes it with such aggressive compounds as sulfurous anhydride, different nitrogen oxides and ozone. These give rise to acid rains and smogs,²¹ which cause deterioration of structural materials (concrete, marble, bricks, polymeric materials, lacquers and paints).

Reactions of polymers with nitrogen oxides constitute an important factor responsible for deterioration of the functions of polymers. Studies on nitration of organic compounds both in the

liquid and gas phases began in the mid-nineteenth century. Both nitric acid and nitrogen oxides were used as nitrating agents. The nitration of aromatic compounds is, as a rule, an ionic process,^{22–24} whereas that of the paraffin hydrocarbons is a free-radical process initiated by nitrogen dioxide, NO₂.^{25–27} In this case, nitric acid served as a source of nitrogen oxides. The addition of small amounts of nitrogen dioxide initiates degenerate branched chain oxidation of hydrocarbons in the liquid phase and, on the other hand, results in chain termination of oxidation reactions.²⁸

Systematic studies of the effect of nitrogen oxides on the stability of polymeric materials began in the late 1950s.^{29–32} The major contribution to the solution of this problem was made by Jellinek who studied degradation of different classes of polymers in an atmosphere of nitrogen dioxide and its dimer at ambient temperatures and under the combined action of nitrogen dioxide, oxygen and near-UV light and visible light.³²

Eight oxides of nitrogen are known; however, only three of them, *viz.*, NO, NO₂ and N₂O₄, are thought to be air pollutants.³³ The atmospheric concentrations of other nitrogen oxides are too low to have a pronounced effect on the ageing of polymers under natural conditions.

The concentrations of nitrogen oxides in the atmosphere are subject to diurnal and seasonal variations over a rather wide range and depend on the position and weather conditions. The maximum permissible concentrations of nitric oxide in urban atmospheres are 2×10^{-8} mol litre⁻¹ (the peak concentration) and 2×10^{-9} mol litre⁻¹ (the daily average concentration). The maximum permissible concentration of nitrogen dioxide is 1.85×10^{-9} mol litre⁻¹ in both cases. In the production areas, the permissible concentration of NO₂ is about 1.1×10^{-7} mol litre⁻¹ (Refs 34, 35).

Nitrogen dioxide always exists in equilibrium with its colourless linear dimer, N₂O₄. The heat of formation of N₂O₄ is -61.4 kJ mol⁻¹ at 298 K.



The equilibrium constant decreases with the increase in the total pressure of NO₂ + N₂O₄ (*P*) and is 0.1415 atm at $P = 4.3 \times 10^{-2}$ atm and $T = 298$ K.³⁶

Based on experimental and calculated data,^{37–40} it was assumed that nitrosation of alkenes in non-polar solvents is the result of the reaction of carbon–carbon double bonds with nitroso nitrate, ON–ONO₂, a less stable isomer of linear N₂O₄.

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[†] Dedicated to the memory of Academician N M Emanuel (1915–1984).

Some additional remarks are to be made before analysing the results of investigations on the reactions of polymers with nitrogen oxides and establishing the possibility of extrapolating them in order to assess the ageing of polymers in a polluted atmosphere. Since the atmospheric concentrations of nitrogen oxides are low, the rates of their reactions are also low. Therefore, the ageing processes due to other factors (*e.g.*, thermal oxidation, photo-initiated oxidation, ozone ageing, biodegradation of polymers *etc.*) can compete with or be more efficient than the reactions involving nitrogen oxides. Therefore, the results of tests under natural conditions can hardly be used for evaluation of the contribution of the processes initiated by nitrogen oxides. These reactions are usually studied at the concentrations of air pollutant gases which are several orders of magnitude higher than their atmospheric concentrations. The results obtained under these conditions are, as a rule, linearly extrapolated to the atmospheric concentrations. Such *a priori* extrapolation is not obvious, since the contributions of particular stages to the overall ageing process under the conditions of accelerated tests can vary depending on the experimental conditions.

Ageing of polymers exposed to nitrogen oxides is due to the reactions of gases diffusing into the polymer with reactive groups of macromolecules. These processes are characterised by non-uniform propagation of the reaction through the bulk of the sample and require complicated description of their kinetics.

'Kinetic inequivalence' of reactants is typical of the chemical reactions in solid polymers.^{2,4} This means that the species with the same chemical structure have different nearest environments and therefore react with different rate constants. As a consequence, the most reactive species are consumed rapidly so that the overall rate constants decrease with time. However, relaxation processes occurring in polymers favour the recovery of the initial distribution of reactivities of the species. Therefore, the reaction kinetics appears to be dependent on the ratio of the rates of chemical reactions and relaxation processes.⁴¹ This also requires a critical view on simple transfer of the results of accelerated tests to the ageing of polymers in atmospheres polluted with nitrogen oxides.

Finally, it should be noted that most of the studies of the effect of nitrogen oxides on polymeric materials involve the determination of changes in the average degree of polymerisation. However, this parameter characterises only one reaction, *viz.*, degradation of macromolecules, though this is of prime importance. A detailed study of degradation in reactions of various polymers with nitrogen dioxide was carried out by Jellinek.³² He has divided all polymers into three main groups differing in stability toward NO₂. In the present review, the results will also be analysed using this classification. Changes in the mechanical properties can be considered as important operating characteristics of a polymer as a structural material; however, this parameter provides no direct information on the chemical transformations and structure of macromolecules. This information can be obtained using IR spectroscopy, but changes in the absorption spectra can usually be detected only at rather high degrees of conversion. Therefore, the use of other physicochemical methods for the analysis of the transformations occurring in the polymers exposed to nitrogen oxides, as well as the analysis of the distribution of the reaction over the bulk of the sample are of crucial importance for the elucidation of complicated mechanisms of these reactions. Sometimes, ageing products can be more reactive towards nitrogen oxides than the initial polymer.

In the present review, we considered the results obtained in studies on the ageing of different classes of polymers by traditional methods of physicochemical analysis and in the investigations of these processes by ESR spectroscopy, which allow one to draw conclusions on free-radical stages of the ageing of polymers involving nitrogen oxides from the structure of stable nitrogen-containing macroradicals produced in the reactions.

II. Reactions of polymers with nitrogen dioxide

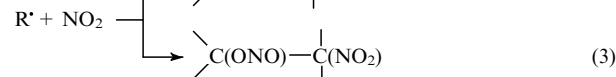
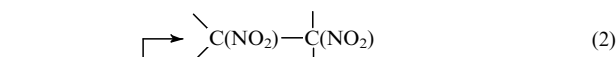
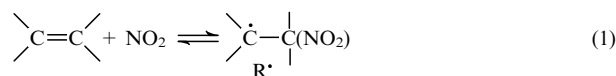
Nitrogen dioxide plays the role of a moderately reactive free radical (the strength of the ONO—H bond is 322 to 326 kJ mol⁻¹),⁴² which can initiate several types of reactions, *e.g.*, hydrogen abstraction from molecules of organic compounds and reversible addition to carbon—carbon double bonds. Additionally, NO₂ and its dimer can enter into specific reactions with functional groups of macromolecules.

1. Carbon-chain polymers containing no carbon—carbon double bonds

Carbon-chain polymers containing no carbon—carbon double bonds in both the main chain and side groups [*e.g.*, polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(methyl methacrylate) (PMMA), polyacrylonitrile (PAN), poly(vinyl chloride) (PVC) and poly(vinyl fluoride) (PVF)] are characterised by insignificant changes in their properties under the conditions of accelerated tests (Jellinek *et al.*^{43,44} carried out their experiments at a NO₂ concentration of 7.8×10^{-3} mol litre⁻¹ and $T = 308$ K; the exposure time was ~ 30 h). Linear extrapolation of the results obtained to the NO₂ concentration typical of polluted atmospheres predicts a long-term stability of the polymers.⁴⁵

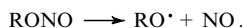
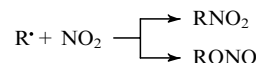
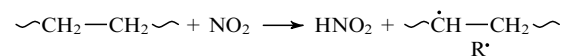
Let us consider the results of investigations of the effect of NO₂ on particular representatives of these polymers in more detail.

Pioneering studies of the reaction of nitrogen dioxide with PE and PP have been carried out by Ogihara *et al.*^{30,31} Using IR spectroscopy, they have found that nitrogen dioxide cannot abstract secondary and tertiary hydrogen atoms from the PE and PP molecules at 298 K. It can only add to the vinyl, vinylene and vinylidene units that are formed in the synthesis of, *e.g.*, PE. These reactions resulted in dinitro compounds and nitro nitrites.



At $T \geq 373$ K, nitro, nitrite, nitrate, carbonyl and hydroxy pendent groups are formed in these polymers.

The following reaction mechanism was proposed:



Subsequent reactions involving the RO^{*} radicals result in macromolecular nitrates, alcohols and carbonyl compounds. This scheme allows rationalisation of the accumulation of the nitro groups, which proceeds at a constant rate, and autoaccelerated formation of nitrates, alcohols and carbonyl compounds; however, it provides no explanation for the S-shaped dependence of the accumulation of nitrites.

The activation energy (E_a) for the NO₂ addition to the double bonds of PE obtained by different methods is 8 to 16 kJ mol⁻¹. The activation energy for hydrogen abstraction lies between 56 and 68 kJ mol⁻¹ for PE and is 60 kJ mol⁻¹ for PP.

At room temperature and NO₂ concentrations lying between 5.4×10^{-4} and 5.4×10^{-3} mol litre⁻¹, the characteristics of PE, PP, PAN and PMMA change only slightly even if they are simultaneously exposed to a combination of NO₂, O₂ and UV radiation.⁴³ The reactions of NO₂ with PVC and PVF resulted in a

slight decrease in the content of chlorine and fluorine atoms, respectively.^{32, 43}

At temperatures between 298 and 328 K, nitrogen dioxide (7.8×10^{-3} – 3.4×10^{-2} mol litre⁻¹) can abstract tertiary hydrogen atoms from PS molecules to form pendent nitro and nitrite groups.³² These reactions proceed at low rates and are accompanied by chain scissions of the macromolecules.^{32, 45, 46} According to Jellinek, the dependence of the decrease in the average degree of polymerisation of PS exposed to NO₂ on the exposure time has three (initial, middle and final) linear regions. A decrease in the apparent degradation rate was observed during the second stage of the reaction (the middle region of the dependence). Presumably, this was related to the association of the macromolecules in solution, which is due to the effect of polar groups and can affect the results of viscosimetric measurements. Subsequent increase in the apparent degradation rate was attributed to the consumption of these nitrogen-containing groups and to a decrease in the degree of association of the macromolecules.

Polystyrene films were also simultaneously exposed to NO₂ (1.1×10^{-4} mol litre⁻¹) and light ($\lambda > 280$ nm).⁴⁶ No polymer degradation was observed in the initial stage (at exposure times of no longer than 10 h). Then chain scissions occurred at a constant rate. After 40 h, degradation ceased. The mechanism of degradation under these conditions was not discussed.

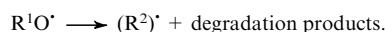
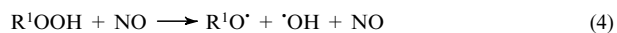
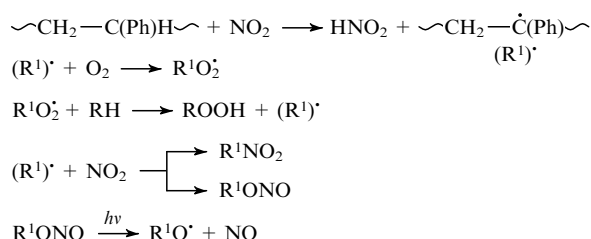
An attempt to carry out a quantitative study of the ageing of PS and poly(*tert*-butyl methacrylate) (PTBMA) under the conditions simulating the ageing of these polymers in an atmosphere polluted with NO₂ has been undertaken by Huber.⁴⁷ Glass supports coated with the samples were exposed to a stream of air containing NO₂ (2.5×10^{-6} to 3.7×10^{-5} mol litre⁻¹) at 300 K and simultaneously irradiated with light ($\lambda > 290$ nm). The number of chain scissions per 10 000 monomer units (α) was determined from the data of viscosimetric measurements. The dependence of α on the exposure time can be described by an empirical equation

$$\alpha = \frac{P}{Q} (\exp Qt - 1),$$

where P and Q are constants and t is time. This equation describes an autocatalytic process. At $Q \rightarrow 0$, degradation occurs at a constant rate. As the thickness of the sample increases, both constants, P and Q , decrease, the former decreasing faster than the latter. Autocatalytic process is more pronounced for thin films. Degradation of thin PS films under the same conditions occurs slower than that of the PTBMA films and its autocatalytic nature is more pronounced. Possible reasons for the dependence of the kinetic parameters of degradation on thickness of the samples have not been considered.

The autocatalytic type of degradation of PTBMA was associated⁴⁷ with the photo-induced formation of isobutylene, which reacts with NO₂, thus initiating free-radical degradation processes of macromolecules.

The IR spectrum of PS exposed to NO₂ and light under conditions mentioned above exhibits two bands at 1686 and 3400 cm⁻¹ corresponding to the carbonyl and hydroxy groups, respectively. The formation of nitrogen-containing products has not been observed in both PTBMA and PS. The following reactions have been assumed⁴⁷ to proceed in PS:



It is believed that the decomposition of hydroperoxides exposed to NO and light [reactions (4) and (5)] leads to autocatalytic degradation of PS.

The results of investigations on the mechanisms and kinetics of the reactions of macromolecular hydroperoxides with nitric oxide are considered in more detail in the forthcoming sections.

2. Reactions of nitrogen dioxide with carbon-chain polymers containing carbon–carbon double bonds

Among the reactions of NO₂ with carbon-chain polymers containing carbon–carbon double bonds, its reactions with rubbers have been studied in most detail. Rubbers are much more susceptible to NO₂ than the polymers containing no double bonds in both the main chain and side groups of the macromolecules. First, this is due to the ability of NO₂ to add reversibly to carbon–carbon double bonds to give nitroalkyl radicals [reaction (1)], thus initiating free-radical transformations of elastomers. Second, it was found⁴⁸ that the rate of the formation of products (Prod) of the liquid-phase reactions of NO₂ with alkenes is described by the equation

$$\frac{d[\text{Prod}]}{dt} = k'[\text{alkene}][\text{NO}_2] + k''[\text{alkene}][\text{NO}_2]^2,$$

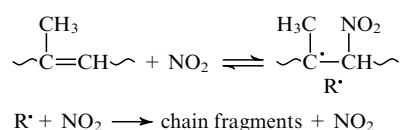
where k' is the effective rate constant for the formation of products in the reactions of allyl radicals with NO₂ and k'' is the effective rate constant for the formation of products in reactions (1)–(3).

The second term of this equation dominates at high NO₂ concentrations; this corresponds to the formation of products in the recombination reactions of nitroalkyl radicals with nitrogen dioxide [reactions (1)–(3)]. The first term of this equation dominates at low NO₂ concentrations; this is associated with the ability of nitrogen dioxide to abstract hydrogen atoms in β -position to the double bond to give allyl radicals, which then combine with an NO₂ molecule. Depending on the structure of the alkene, the reaction resulting in the formation of the allyl radical can be either weakly exothermic or weakly endothermic. For instance, the strengths of the weakest C–H bonds in the structural fragment $-\text{C}(1)\text{H}_2-[\text{C}(2)\text{H}_3]\text{C}=\text{CH}-\text{C}(3)\text{H}_2-$ of synthetic isoprene rubber are 334, 351 and 316 kJ mol⁻¹ for the C(1)–H, C(2)–H and C(3)–H bonds, respectively.⁴⁹

In preliminary studies it was shown⁴³ that exposure of polyisoprene and polybutadiene to nitrogen dioxide leads to both degradation and cross-linking of the macromolecules, whereas butyl rubber (a copolymer of isobutylene with 1.75% of isoprene) only undergoes degradation. Jellinek *et al.*^{32, 50, 51} carried out a detailed study of the ageing of butyl rubber exposed to (i) NO₂ (5.2×10^{-7} to 5.2×10^{-5} mol litre⁻¹) alone, (ii) an NO₂–O₂ mixture and (iii) an NO₂–O₂ mixture plus UV light ($\lambda > 280$ nm). It was found that in the first case the polymer degradation is described by the formula

$$\alpha = k_{\text{ef}}t,$$

where k_{ef} depends on the NO₂ pressure. This equation is valid except for the initial portion of the curve where the reaction rate decreases with time. A kinetic scheme of the main-chain scission was proposed.



Exposure to a mixture of O₂ (6.8×10^{-4} to 7.8×10^{-3} mol litre⁻¹) and NO₂ (5.2×10^{-7} to 5.2×10^{-5} mol litre⁻¹) leads to an increase in the degradation rate of the

rubber with the increase in the concentrations of both gases. According to Jellinek, there are three factors governing the main-chain scissioning in the polymers exposed to O_2 – NO_2 mixtures. These are (i) degradation induced by NO_2 alone, (ii) oxidative degradation of macromolecules and (iii) scissions of macromolecules owing to the synergistic effect of NO_2 and O_2 , which in turn is due to the NO_2 -induced decomposition of hydroperoxides formed in the reaction.

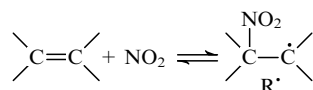
According to Jellinek, the degradation kinetics of butyl rubber exposed to NO_2 – O_2 mixture and UV irradiation is described by the following equation:

$$\alpha = k'_{ef}t^2 + k''_{ef}[NO_2][1 - \exp(-k'''t)],$$

where k' and k'' are the effective rate constants for different groups of reactions and k''' is the rate constant for degradation of the elastomer exposed to NO_2 alone. At low NO_2 pressures, the degradation rate increases with time. At high NO_2 pressures, the reaction slows down.

3. ESR studies of the reactions of nitrogen dioxide with double bonds in solid polymers

As was mentioned above, nitration of aromatic compounds usually follows an ionic mechanism, whereas nitration of aliphatic compounds (in particular, the reaction of NO_2 or its dimer with carbon–carbon double bonds in non-polar media) proceeds by free-radical mechanism.^{37, 48, 52, 53} Liquid-phase reactions of low-molecular-mass alkenes with NO_2 – N_2O_4 mixture produce paramagnetic centres.⁵⁴ It was found that the ESR spectra arising are temperature-dependent and that their parameters differed from those of the spectra of nitroalkyl radicals. These spectra were associated with the π -complexes formed in the reactions of nitrogen dioxide with the double bonds of alkenes. Nitroalkyl radicals produced in the styrene– NO_2 (or α -methylstyrene– NO_2) systems were identified by Kommandeur *et al.*⁵⁵ in the ESR spectra of the spin adducts of these radicals with nitrosobenzene. Paramagnetic centres observed⁵⁴ were assigned to the nitroxyl radicals generated in the reactions



It is believed that reaction (6) is due to the trace amounts of NO in nitrogen dioxide. Analysis of this scheme shows that the formation of nitroxyl radicals (7) must be autoaccelerated. This was confirmed in further studies.⁵⁶

a. Reactions of UV-irradiated poly(methyl methacrylate) with nitrogen dioxide

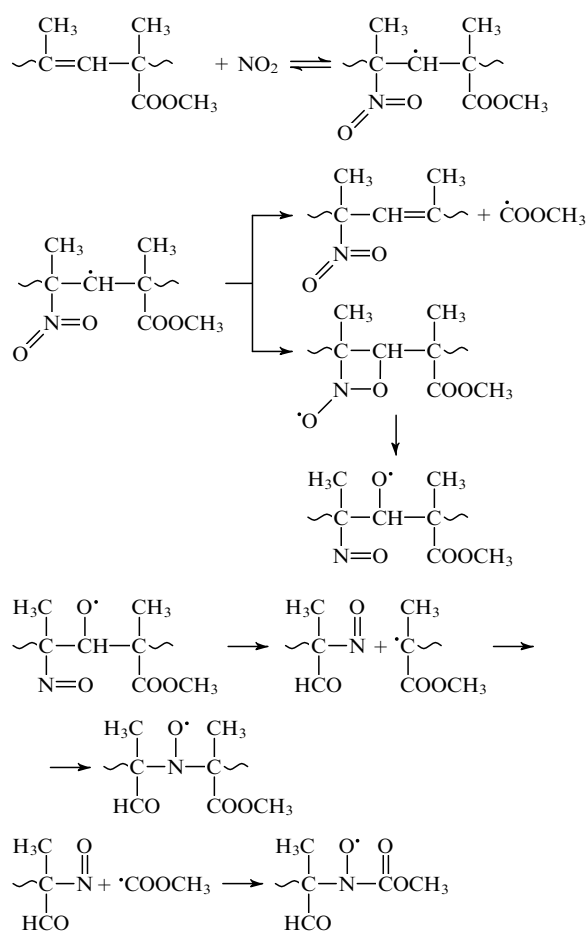
Nitrogen dioxide virtually does not react with PMMA. On the other hand, it is known that irradiation of this polymer with UV light causes elimination of the ester groups leading mainly to methyl formate, $HCOOCH_3$, and macromolecular structures containing double bonds in the main chain.⁵⁷ The reaction of nitrogen dioxide with the double bonds formed must initiate free-radical ageing reactions in the polymer.

The formation of paramagnetic species in PMMA containing 0.3 – 0.4 mol kg^{-1} of the $\sim(CH_3)C(COOCH_3)-CH=C(CH_3)-CH_2\sim$ units (produced upon photolysis) under the action of NO_2 has been studied by ESR spectroscopy.⁵⁸ The experimental ESR spectrum of the solid polymer is a superposition of two anisotropic triplets typical of dialkylnitroxyl and acylalkylnitroxyl radicals in the solid phase with low frequencies of rotational motions.^{59, 60} Dialkylnitroxyl macroradicals $R-N(O^{\bullet})-R$ give an anisotropic triplet with $A_{||}^N = 3.2 \pm 0.1$ mT and $g_{||} = 2.0026 \pm 0.0005$, while the triplet corresponding to acylalkylni-

troxyl radicals $RC(=O)-N(O^{\bullet})-R$ is characterised by the parameters $A_{||}^N = 2.1 \pm 0.1$ mT and $g_{||} = 2.0027 \pm 0.0005$. In a benzene solution of PMMA, these radicals exhibit triplet ESR spectra with the parameters $a^N = 1.5 \pm 0.1$ mT, $g = 2.0064 \pm 0.0005$ and $a^N = 0.8 \pm 0.1$ mT and $g = 2.0065 \pm 0.0005$, respectively. The absence of an additional hyperfine splitting in the spectra of these radicals indicates that the carbon atoms neighbouring to the $NO^{\bullet}$ group are tertiary.

The accumulation of dialkylnitroxyl macroradicals occurs without an induction period and its initial rate is proportional to the concentration of nitrogen dioxide in the gas phase.

The kinetics observed shows that the scheme of the formation of dialkylnitroxyl radicals [reactions (1), (6) and (7)] in the liquid phase (see above) is inapplicable to the solid polymer due to the low probability of the encounter of a macroradical with the macromolecular nitroso compound. It was assumed that these radicals are produced as a result of a series of 'pseudocage' reactions such as those shown below:



According to this scheme, the NO_2 group and the free valence are localised on the neighbouring carbon atoms of the primary nitroalkyl radical and can react with each other to produce unstable, four-membered alkoxyalkylnitroxyl radicals, which decompose to give the alkoxy radical and nitroso group at the adjacent carbon atom. Subsequent decomposition of the alkoxy radical macroradical results in an alkyl radical and nitroso compound located in the immediate vicinity of each other. The reaction between them, resulting in the formation of a dialkylnitroxyl macroradical, can be initiated by small-amplitude translational and rotational motions. Acylalkylnitroxyl radicals appear in the reactions of the low-molecular-mass methoxycarbonyl radicals with tertiary nitroso compounds. This reaction scheme ignores concurrent transformations of reactive free radicals, which proceed without formation of nitroxyl radicals. These processes seem to be responsible for the low yield of $R-N(O^{\bullet})-R$ radicals

(about one hundredth of the total number of consumed NO_2 molecules).

The ability of nitro compounds to undergo reduction to nitroso compounds through the stages of formation and decomposition of alkoxyalkylnitroxyl radicals in the liquid phase has been pointed out.^{61–63}

It was also concluded that the reaction between the double bonds of PMMA and NO_2 is accompanied by chain scissions in the macromolecules and elimination of the ester side groups.⁵⁸ In addition, the structure of the nitroxyl macroradicals produced suggests that NO_2 is added not only to the less sterically shielded carbon atom of the double bond, but also to the neighbouring atom. This was also observed in the liquid-phase reaction of methyl methacrylate with nitrogen dioxide.⁶⁴

b. Nitroxyl radicals produced in reactions of nitrogen dioxide with rubbers

As was mentioned in the preceding Section, macromolecular nitroxyl radicals produced in the reactions of NO_2 with the double bonds of polymers are spin labels which carry information on macromolecular dynamics. Knowledge of the formation rules and structure of nitroxyl radicals allows elucidation of the mechanisms of macromolecular transformations in the polymers.

This approach was used⁶⁵ to obtain spin-labelled macromolecules of 1,4-*cis*-polyisoprene (synthetic isoprene rubber, or SKI[®]) and a copolymer of ethylene, propylene and dicyclopentadiene (SKEPT-40[®]). These spin labels were used to study the macromolecular dynamics in solid SKI[®] and the structure of the reaction front during nitration of the polymer.⁶⁶

Nitroxyl macroradicals formed in these polymers at 293 K exhibit nearly identical ESR spectra. The ESR spectrum of nitroxyl radicals in SKI[®] recorded at 298 K is shown in Fig. 1*a*. It is an anisotropic triplet with $A_{\parallel}^N = 3.10$ mT and $g_{\parallel} = 2.0028 \pm 0.0005$. This indicates that the correlation time, τ_c , of rotational motions at this temperature is longer than 10^{-9} s. As the temperature increases, the spectra become triplets with $a^N = 1.53 \pm 0.03$ mT and $g = 2.0057 \pm 0.0005$ (Fig. 1*b*), which indicates a substantial shortening of the correlation time. The change in τ_c in the temperature interval from 293 to 373 K (Fig. 2) is described by the equation

$$\tau_c = \tau_0 \exp\left(\frac{E}{RT}\right),$$

where $\log \tau_0 = -14.2$ and E is the activation energy for rotational diffusion (34.7 kJ mol⁻¹).

These values are close to the corresponding values determined for SKI[®] using a bulky spin probe.⁶⁷

Studies on the kinetics of the formation of nitroxyl radicals in solid elastomers showed that free-radical transformations of double bonds in the presence of nitrogen dioxide differ fundamentally from analogous liquid-phase reactions.⁵⁶

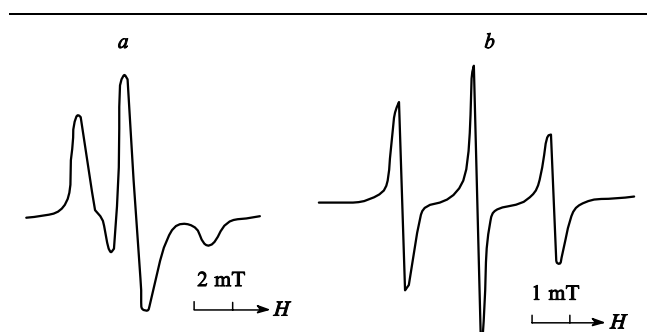


Figure 1. ESR spectra of nitroxyl macroradicals produced in the reaction of nitrogen dioxide with SKI[®]-3M at 293 (*a*) and 373 K (*b*).

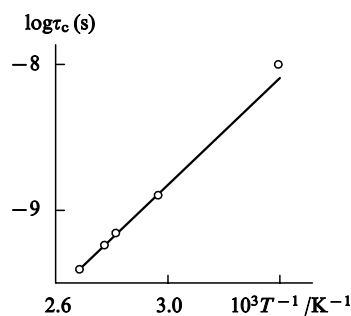


Figure 2. Temperature dependence of the correlation time τ_c of rotational diffusion of SKI[®] macromolecules measured using spin labels obtained in the reaction of polyisoprene with nitrogen dioxide.

The changes in the concentration of nitroxyl radicals as functions of the nitration time of SKI[®] at different concentrations of nitrogen dioxide in the gas phase are shown in Fig. 3*a*. As in the case of PMMA, these radicals are formed in an NO_2 - N_2O_4 atmosphere without an induction period and the initial rate of formation is proportional to the concentration of nitrogen dioxide. Initially, the concentration of radicals increases and reaches a maximum value at $[\text{NO}_2] = (7-8) \times 10^{-4}$ mol litre⁻¹ and then decreases. It was assumed that this shape of the kinetic curves is due to the loss of nitroxyl radicals in the trapping reactions and in the redox reactions involving the nitrogen dioxide dimer.

A long induction period is observed in the presence of O_2 in the gas mixture (Fig. 3*b*, curve 2). The apparent accumulation rate of radicals to the end of this period is 50 to 60 times lower than that in the absence of oxygen at the same NO_2 concentration; however, the amount of radicals accumulated is three times as large as that

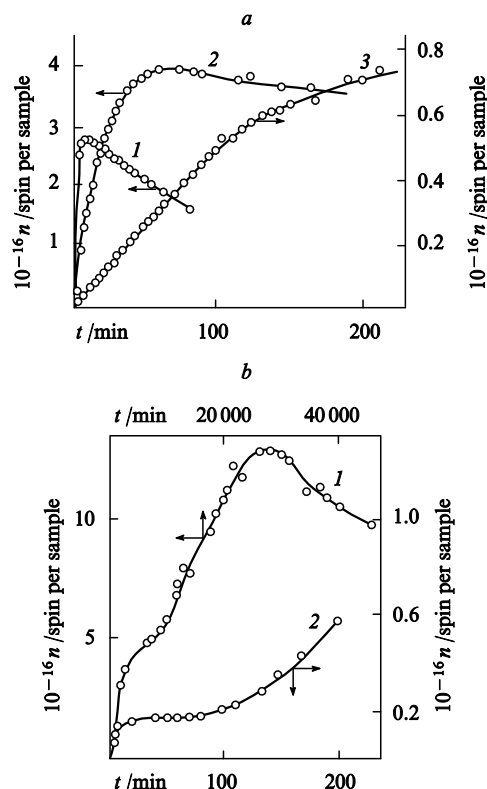


Figure 3. Kinetic curves of accumulation of nitroxyl macroradicals in SKI[®] exposed to NO_2 (*a*) and an NO_2 - O_2 mixture (*b*); (*a*): $[\text{NO}_2]$ /mol litre⁻¹: 2.2×10^{-3} (1), 7×10^{-4} (2) and 10^{-5} (3); (*b*): kinetic curve (1) and the initial portion of curve 1 (2); $[\text{NO}_2] = 7 \times 10^{-4}$ mol litre⁻¹ and $[\text{O}_2] = 1.2 \times 10^{-2}$ mol litre⁻¹.

accumulated in the former case. It was concluded that in the absence of O_2 nitroxyl macroradicals are formed in two ways. The first mechanism is the same as the liquid-phase one, while the second is a 'pseudocage' mechanism, which predominates if the reaction is carried out in the absence of oxygen. In the presence of O_2 , 'pseudocage' reactions are inhibited due to the conversion of initially formed nitroalkyl macroradicals into nitroperoxide radicals. From these data it also follows that the recombination of nitroxyl macroradicals with nitroalkyl and allylic macroradicals in the absence of O_2 must lead to gradual cross-linking of the SKI[®] macromolecules.

Similar kinetics of accumulation of nitroxyl macroradicals was also observed for SKEPT-40[®], which differs from SKI[®] by a substantially lower proportion of double bonds.

The mechanism of formation of nitroxyl radicals in these polymers by the 'pseudocage reactions' is in essence the same as that in the case of PMMA containing double bonds. Alkoxyl macroradicals produced in the 'pseudocage reactions' cause degradation of polymers, while recombination of nitroxyl radicals with nitroalkyl radicals leads to cross-linking of the elastomer.

Reactions of NO_2 with solid polymers can be considered as the interaction between the molecules diffusing from the gas phase and reacting in the bulk of the polymer. In this case, a non-uniform distribution of the reaction front in the bulk of the polymer must be present. The method of ESR tomography (or the ESR imaging technique),^{68–70} which has been rapidly developed recently, allows determination of the spatial distribution of paramagnetic species. In the case of reaction of NO_2 with the double bonds of elastomers, the spatial distribution of nitroxyl macroradicals characterises the structure of the reaction front during nitration of the polymers.

The results of investigations of the reactions of SKI[®] with NO_2 and NO_2 – O_2 mixtures by ESR tomography have been reported.⁶⁶ The spatial distributions of nitroxyl macroradicals in the initial and deep stages of the nitration of SKI[®] by a NO_2 – N_2O_4 mixture are shown in Fig. 4a and Fig. 4b, respec-

tively. As can be seen, after the initial 2.5 h the reaction front penetrates the surface of the polymer to a depth of ~ 1 mm. The interior of the sample is inaccessible to nitrogen dioxide. As the reaction time is extended to 740 h, the depth of the reaction zone increases only by 20% to 30%. The extent of the reaction is maximal in the near-surface layer and decreases as the reaction front moves deeper into the sample. The results obtained show that the initial structure of the reaction front is due to the penetration of NO_2 into the bulk of the sample along pores, cracks, sites with low local density and that further propagation of the reaction front is very slow. Studies of the rates of diffusion of the low-molecular-mass radical (2,2,6,6-tetramethyl-4-oxopiperidinoxyl) from the gas phase into the bulk of an SKI[®] sample nitrated for different periods of time showed that nitration was accompanied by the efficient formation of a three-dimensional network structure, which precludes the diffusion of low-molecular-mass compounds into the sample.

When an SKI[®] sample is exposed to an NO_2 – N_2O_4 – O_2 mixture, the limitations on diffusion due to the changes in the structure of the polymer must diminish since the concentration of cross-links decreases in the presence of oxygen. Therefore, one could expect a greater depth of the reaction zone and a more uniform distribution of nitroxyl macroradicals in the bulk of the polymer. In fact, the distribution of nitroxyl macroradicals in the bulk of the sample and its change during nitration of the samples with an NO_2 – O_2 mixture (Fig. 4c,d) are similar to those for the sample exposed to an NO_2 – N_2O_4 mixture, but the reaction zone penetrates the sample to a smaller depth. This can likely be rationalised by the fact that the structure of the reaction front is due to the membrane-like type of the process.⁷¹ Under these conditions, the propagation velocity of the reaction front is determined by the consumption rate of nitroalkyl macroradicals: the higher the consumption rate, the smaller the depth to which the reaction front penetrates. Introduction of O_2 into the system causes an increase in the consumption rate of nitroalkyl radicals, thus decreasing the depth of the reaction front. Thus, the results obtained by ESR tomography showed that if rubbers are exposed to high NO_2 concentrations, the degradation and cross-linking of macromolecules occur in the narrow (of the order of 1 mm thick) surface layer and that no modification occurs in the bulk of the polymer sample for long.

4. Reactions of nitrogen dioxide with polyamides, polyurethanes and polyamidoimides

a. Effect of nitrogen dioxide on aliphatic polyamides

Polymers containing amide and urethane groups form a particular class of materials sensitive to NO_2 . Jellinek *et al.*^{72,73} showed that exposure of nylon-66 films of different morphology to NO_2 (2.6×10^{-5} to 10.4×10^{-5} mol litre⁻¹) causes main-chain scission in the polymers. The degradation of nylon is a diffusion-controlled reaction. Its rate and depth depend essentially on the degree of crystallinity of specimens and on the size of crystallites. The reaction can be inhibited by small amounts of benzaldehyde or benzoic acid. The degradation is accelerated in the presence of air and UV light in addition to NO_2 . It is believed that benzoic acid blocks the amide groups and that only a few of them, not involved in hydrogen bonding, enter into the reaction. The following mechanism for the polymer degradation under the action of NO_2 was proposed.

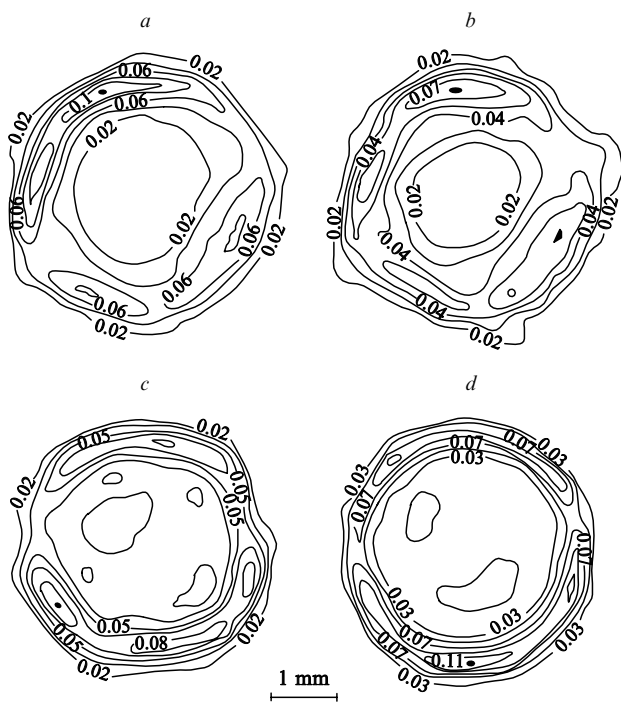
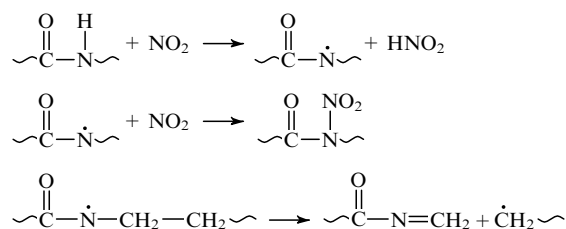
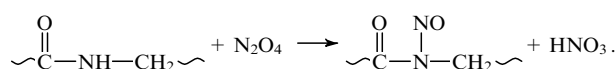


Figure 4. Bulk distribution of nitroxyl macroradicals produced upon nitration of SKI[®] by NO_2 with a concentration of 3.8×10^{-4} mol litre⁻¹ (a, b) and a mixture of NO_2 (5.5×10^{-4} mol litre⁻¹) with O_2 (1.5×10^{-3} mol litre⁻¹) (c, d). Nitration time/h: 2.5 (a), 720 (b), 168 (c) and 505 (d). It should be remembered that NO_2 always is in equilibrium with N_2O_4 .

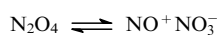
The effect of nitrogen dioxide on nylon fibres has been studied.⁷⁴ It was found that long-term storage of samples in an atmosphere with low NO₂ concentration at room temperature did not lead to their darkening or to a decrease in the tensile strength. These characteristics deteriorated at elevated temperatures. Degradation of nylon fibres irradiated with UV light in air was more pronounced in the presence of nitrogen oxides.

The results of the UV, IR and ESR studies on the ageing of polycapramide (PCA) in a nitrogen dioxide atmosphere have been reported.⁷⁵ The absorption bands in the region of 390–435 nm typical of *N*-nitroso amides were observed in the UV spectra of PCA films stored in an NO₂ atmosphere.⁷⁶ IR studies showed that the intensity of the band at 3293 cm⁻¹ assigned to the stretching vibrations of hydrogen-bonded N–H groups decreases on storage of thin PCA films in an NO₂ (4 × 10⁻⁵ to 4 × 10⁻⁴ mol litre⁻¹) atmosphere. The intensities of the bands at 1642 and 1563 cm⁻¹ also decrease. A band at 1730 cm⁻¹ characteristic of the stretching vibrations of the C=O groups not involved in hydrogen bonding appears instead of these bands, as well as two bands, at 1504 and 1387 cm⁻¹, corresponding to the antisymmetrical and symmetrical stretching vibrations of the –N=O groups of nitroso amides. It was found that under these conditions the initial rate of the nitrosation of PCA is proportional to [NO₂]^{*n*}, where *n* ≈ 2. The formation of the nitroso amide groups can be depicted as follows:

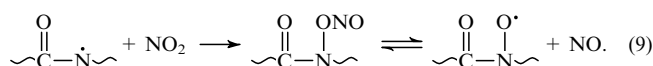
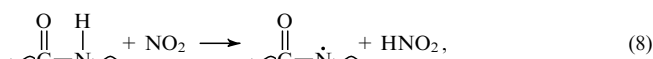


Nitrosation of PCA leads to disappearance of the system of hydrogen bonds, which determines its mechanical properties. After exposure to NO₂, the PCA films degraded at minimum mechanical actions.

White^{77,78} carried out detailed studies of the liquid-phase reactions of low-molecular-mass amides with nitrogen dioxide. He suggested that the action of N₂O₄ used as the nitrosating agent is due to the equilibrium



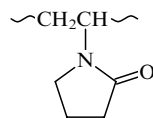
and that the reaction proceeds by an ionic mechanism. Jellinek *et al.*^{72,73} proposed a free-radical mechanism of the interaction of polyamides with NO₂, which implies the formation of an *N*-nitro amide with a characteristic IR absorption band at 1580 cm⁻¹ as the main product. However, no formation of this product was detected, probably, due to the low proportion of the free-radical reactions in the overall process. The formation of amidyl radicals was confirmed by the accumulation of acylalkylnitroxyl macroradicals (which occurs without induction period, however).⁷⁵ These macroradicals are generated in the reactions



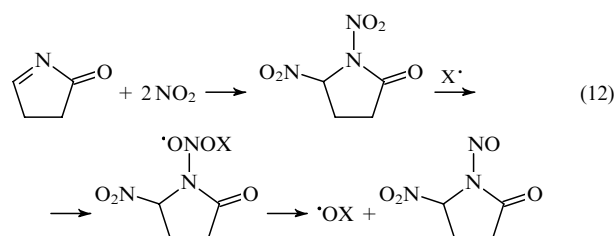
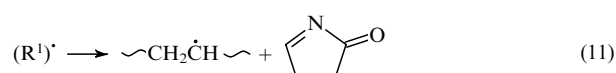
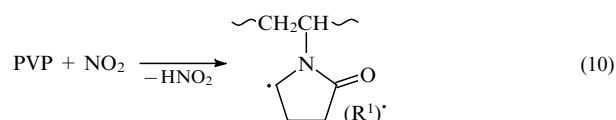
Thus, there are two concurrent mechanisms for the transformation of polyamides in the presence of nitrogen dioxide, namely, the free-radical mechanism with the rate proportional to the concentration of NO₂ and the ionic mechanism, the rate of which is proportional to the square of the NO₂ concentration. The ratio of these processes depends on the concentration of nitrogen dioxide in the gas phase. Therefore, linear extrapolation of the results obtained under the conditions of accelerated tests cannot be used for predicting the stability of polyamides.

b. The effect of nitrogen dioxide on polyvinylpyrrolidone

Polyvinylpyrrolidone (PVP) is a carbon-chain polymer containing a tertiary amide group in the pendent ring.



The interaction of PVP with NO₂ has been described.⁷⁵ Two absorption bands, at λ_{max} = 413 and 435 nm, were observed in the UV spectra of products of the reaction of NO₂ with PVP. As in the case of PCA, these peaks can be assigned to the absorption of the nitroso amide groups N(NO)–C(=O)–(CH₂)₃ formed in PVP due to the elimination of the side cyclic fragments.



X is a free radical.

ESR studies of the reaction of NO₂ (10⁻⁴ to 10⁻³ mol litre⁻¹) with PVP revealed two additional mechanisms for the transformation of the polymer.

The ESR spectrum of paramagnetic species formed in this polymer (Fig. 5) is a superposition of the signals of iminoxyl and acylalkylnitroxyl radicals with the parameters *A*_{||}^N = 4.33 mT, *A*_⊥^N = 2.44 mT, *g*_{||} = 2.0029 and *g*_⊥ = 2.0053 and *A*_{||}^N = 1.94 mT and *g*_{||} = 2.003, respectively.

The iminoxyl radicals are produced as follows. Nitric oxide recombines with (R¹)[•] to give nitroso compounds which undergo

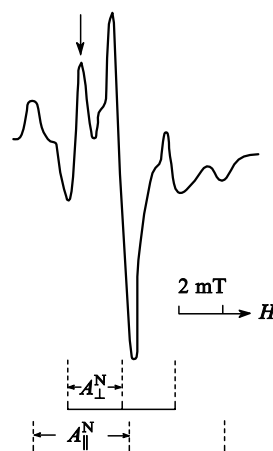
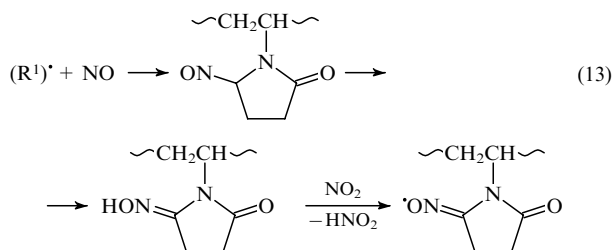
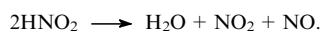


Figure 5. The ESR spectrum of paramagnetic species formed in the reaction of PVP with nitrogen dioxide. The low-field component of the hyperfine structure of acylalkylnitroxyl macroradicals is shown by an arrow.

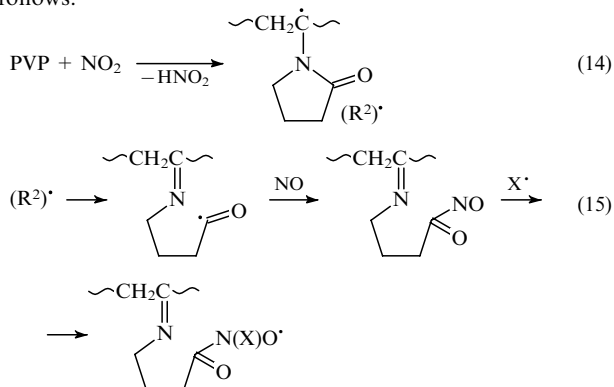
isomerisation into oximes to produce iminoxyl radicals in the reaction with NO_2



Nitrous acid is the source of nitric oxide in the system



The formation of acylalkylnitroxyl radicals can be represented as follows.



It was found that the kinetics of the accumulation of iminoxyl and acylalkylnitroxyl radicals are different. The concentration of iminoxyl radicals increases initially (the rate of accumulation decreases with time), reaches a maximum value and then decreases. The accumulation of acylalkylnitroxyl radicals occurs initially in an autoaccelerated manner and then the rate of the process decreases and the concentration of the radicals reaches a constant value. This indicates that nitrogen-containing radicals are produced from different precursors following reactions with different rate-limiting stages. It was found that the structure and properties of the matrix affect the relative rates of the formation of nitrogen-containing radicals in PVP samples filled with aerosil.⁷⁹

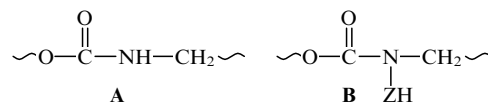
Thus, one can conclude that the presence of tertiary amide groups in the monomer units of PVP leads to weakening of the C–H bonds in the >CH- and $-\text{CH}_2-$ groups neighbouring to the nitrogen atom. Nitrogen dioxide can abstract hydrogen atoms from these groups with ease to produce macroradicals which decompose with the cleavage of the C–C bonds in the β -position to the free valence. Alkyl macroradicals also recombine with nitrogen oxides to give nitrites, nitrates and nitroso compounds and then nitroxyl macroradicals. Trapping of the alkyl macroradicals $(\text{R}^1)^{\bullet}$ and $(\text{R}^2)^{\bullet}$ by the nitroso compounds and nitroxyl radicals must be accompanied by cross-linking of the macromolecules.

c. Reactions of NO_2 with polyurethanes

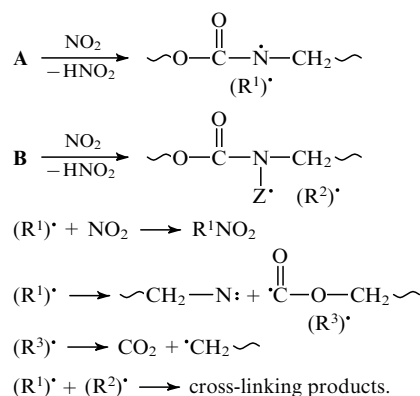
Jellinek *et al.*^{80,81} studied the effect of NO_2 on films of linear polyurethane (PU) synthesised from tetramethylene glycol and hexamethylene diisocyanate. It was found that the degradation of PU is accompanied by cross-linking of macromolecules and that the degree of degradation and the yield (the weight percentage) of the gel fraction are complex functions of the exposure time. For instance, the yield of the gel fraction initially increases up to 20% and then decreases down to nearly zero at 333 K and a NO_2 concentration of 10^{-3} mol litre⁻¹. The number of chain scissions in the sol fraction (*i.e.*, the degree of degradation) increases initially, then decreases and eventually increases again; however, the final degradation rate is lower than the initial one. Exposure of

the PU films to NO_2 is accompanied by evolution of CO_2 , which is a monotonic function of the exposure time. The IR spectra of the films allow assessment of the consumption of the NH bonds ($\nu = 3300$ cm⁻¹).

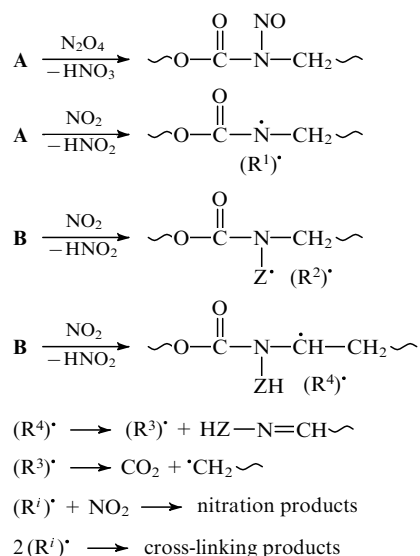
The reaction mechanism proposed by Jellinek *et al.*^{80,81} involves the abstraction of hydrogen atoms from two types of structures, namely, a carbamate structure (A) and a tertiary amido structure (B)



where Z is a side alkyl group, as the initial step. The mechanism involves the following main stages:



According to Jellinek, recombination of the $(\text{R}^1)^{\bullet}$ and $(\text{R}^2)^{\bullet}$ radicals leads to cross-linking of the polymer chains, while decomposition of the $(\text{R}^1)^{\bullet}$ radicals results in the degradation of macromolecules and evolution of CO_2 . Energetically, the decomposition of the $(\text{R}^1)^{\bullet}$ radicals seems to be hardly probable since this reaction results in the terminal macroradical $(\text{R}^3)^{\bullet}$ and a nitrene, which is a very reactive species. On the other hand, more probable decomposition reactions of $(\text{R}^1)^{\bullet}$ involving cleavage of the C–C or C–O bonds produce no alkoxy carbonyl macroradicals $(\text{R}^3)^{\bullet}$, which can undergo decarboxylation (see Ref. 82). Taking into account the mechanisms of the reaction of nitrogen dioxide with aliphatic polyamides and PVP, the ageing of PU in an NO_2 atmosphere can be represented as follows:



$i = 1-4$.

This scheme allows a rationalisation of the degradation accompanied by cross-linking of macromolecules, the consump-

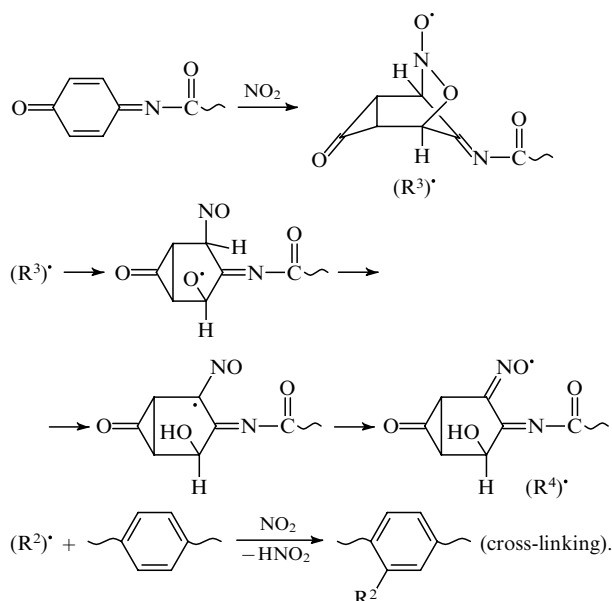
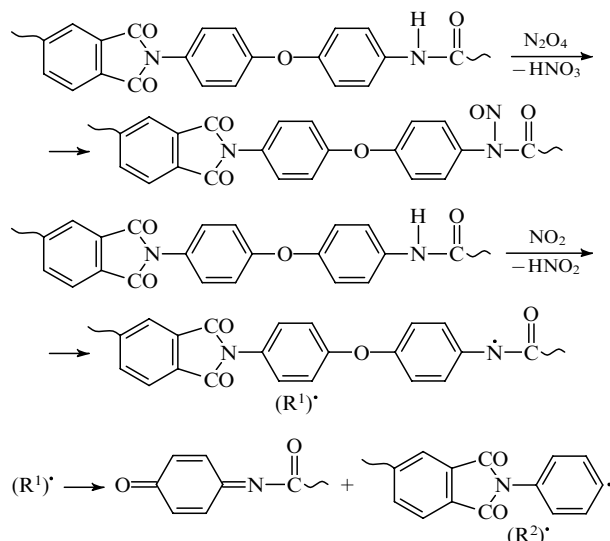
tion of NH groups of the polymer as well as the evolution of carbon dioxide upon degradation.

d. The reaction of NO₂ with a polyamidoimide

The effect of NO₂ on the mechanical properties of a polyamidoimide (PAI) obtained by the polycondensation of chloroformylphthalic anhydride with 4,4'-diaminodiphenyl ether has been studied.⁸³ The experiments were carried out at 323 K and an NO₂ concentration of 5×10^{-3} mol litre⁻¹ and involved the measurements of the temperature dependence of the storage modulus E' and the loss modulus E'' for different exposure times of the PAI samples to NO₂. At 473 K, the parameter E' revealed a non-monotonic decrease and the strongest temperature dependence. An increase in E' at the glass transition temperature (~ 563 K) was observed for the films exposed to NO₂ over a period of eight days. When studying the temperature dependences of the loss moduli E'' of the films exposed to NO₂ for different times, an absorption peak was found to appear at 473 K, which indicates degradation of polymers. All these facts were associated with degradation accompanied by cross-linking of macromolecules.

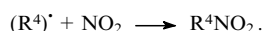
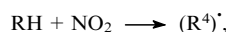
A decrease in the band intensities of the stretching vibrations of the N–H bonds and the appearance of the peaks associated with the addition of NO₂ groups to macromolecules was observed in the IR spectra of the PAI films. No reaction mechanisms were discussed.

To elucidate possible reaction mechanisms, we carried out ESR studies of the effect of NO₂ (10^{-3} mol litre⁻¹, at 293 K) on PAI of the same structure as that of the polymer studied by Kambe and Yokota.⁸³ Under these conditions, iminoxyl radicals with the ESR spectral parameters $A_{\parallel}^N = 4.1$ mT, $A_{\perp}^N = 2.1$ mT and $g_{\parallel} = 2.0028$, $g_{\perp} = 2.0058$ are mainly produced in PAI. The proportion of the acylalkylnitroxyl macroradicals which have nearly the same ESR spectral parameters as those of polyamide and are likely produced by the same mechanism [reactions (8) and (9)] is less than 35%. Formation of iminoxyl radicals in this system is quite unexpected. A conventional mechanism of their formation [reactions of the types (10) and (13) in PVP] involves (i) hydrogen abstraction from the CH₂ group of a molecule, (ii) NO addition to the radical produced and (iii) isomerisation of the newly formed nitroso compound into an oxime. Abstraction of labile hydrogen atoms from the oxime molecules by NO₂ results in iminoxyl radicals. Since the PAI molecules contain no CH₂ groups, this mechanism is impossible. It was assumed that the spin density in the amidyl radicals produced is partially delocalised over the phenyl ring, which facilitates cleavage of the polymer ether bond. The following mechanism of the reaction of NO₂ with PAI was proposed.



Decomposition of the radicals (R¹)^{*} leads to the scission of the main chain of PAI, while their reactions with NO₂, as in the case of PCA, result in acylalkylnitroxyl radicals. The reaction of the radicals (R²)^{*} with the phenyl rings of neighbouring macromolecules causes cross-linking of the polymer and the reaction with NO₂ results in the appearance of NO₂ groups in the sample.⁸³

Kinetic curves of the accumulation of the iminoxyl radicals correspond to the following overall reactions



Their transformation in the coordinates of the following equation

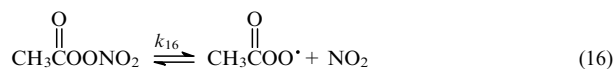
$$\ln \frac{[(\text{R}^4)^{\cdot}]_s}{[(\text{R}^4)^{\cdot}]_s - [(\text{R}^4)^{\cdot}]} = \frac{W_0 t}{[(\text{R}^4)^{\cdot}]_s},$$

where $[(\text{R}^4)^{\cdot}]$ and $[(\text{R}^4)^{\cdot}]_s$ are the current and steady-state concentrations of the radicals, respectively, and W_0 is the rate of formation of the iminoxyl radicals, allows the minimum degradation rate of the polymer, W_d , to be determined from the accumulation of the iminoxyl radicals; W_d was found to be 10^{-8} mol kg⁻¹ s⁻¹. The mechanism proposed allows a rationalisation of the degradation accompanied by cross-linking of the PAI macromolecules as well as the introduction of the NO₂ groups.⁸³

5. On the possibility of polymer degradation resulting from the reaction of nitrogen dioxide with peroxy macroradicals

As was mentioned above, at room temperature nitrogen dioxide can (i) abstract labile hydrogen atoms from macromolecules to produce alkyl or allyl macroradicals and (ii) add to the double bonds, thus producing the nitroalkyl macroradicals. If the reaction is carried out in air, carbon-centred macroradicals are oxidized to give peroxy radicals. Presumably, the reactions of the latter with NO₂ must result in relatively unstable peroxy nitrates, ROONO₂, similarly to the low-molecular-mass radicals $\text{RO}_2^{\cdot}$.^{84–86}

Decomposition of peroxyacetyl nitrate, $\text{CH}_3\text{C}(=\text{O})\text{OONO}_2$, was studied in detail and two mechanisms were considered.^{87,88}



Using the spin trap technique, it was shown that peroxyacetyl nitrate decomposes mainly following reaction (16), which is reverse to the formation reaction of $\text{CH}_3\text{C}(=\text{O})\text{OONO}_2$.⁸⁹ An analogous conclusion was also drawn based on the results of quantum-chemical calculations.⁹⁰ Stabilities and transformation mechanisms of other low-molecular-mass peroxy nitrates have been much less studied.

The thermal stability of products of the reactions of NO_2 with internal $\sim\text{CF}_2\text{CF}(\text{OO}^\bullet)\text{CF}_2\sim (\text{R}_{\text{in}}\text{O}_2^\bullet)$ and terminal $\sim\text{CF}_2-\text{CF}_2-\text{OO}^\bullet (\text{R}_{\text{t}}\text{O}_2^\bullet)$ peroxy macroradicals of poly(tetrafluoroethylene) (PTFE) produced under the action of penetrating radiation or UV light in an O_2 atmosphere was studied by ESR spectroscopy.⁹¹ These macroradicals are stable at $T \leq 333$ K but can enter into reactions with nitrogen dioxide.

If the reaction of the type (16) is the only way of the transformation of peroxy nitrates into PTFE, complete regeneration of the initial peroxy macroradicals must be observed *in vacuo*. The alkoxy macroradicals produced by the reaction (17) can undergo effective decomposition accompanied by scission of the main chain of the polymer.⁹² For instance,



The reaction of terminal alkyl macroradicals with NO_3 or NO_2 results in the formation of stable products and in a decrease in the degree of regeneration of $\text{RO}_2^\bullet$.

It was found⁹¹ that $\text{R}_{\text{in}}\text{OONO}_2$ do decompose with partial regeneration of $\text{R}_{\text{in}}\text{O}_2^\bullet$ at room and elevated temperatures. At 298 K, the peroxy nitrate molecules which undergo dissociation are kinetically inequivalent. At 313 K, they undergo a unimolecular decomposition with a rate constant of the reaction of the type (16), $4.0 \times 10^{-4} \leq k_{16} \leq 4.8 \times 10^{-4} \text{ s}^{-1}$ (Fig. 6a), which is

independent of either $[\text{R}_{\text{in}}\text{O}_2^\bullet]_0$ or the exposure time (t^*) of the samples to nitrogen dioxide. The effective constant k_{16} obtained is about three orders of magnitude smaller than the rate constant for decomposition of $\text{CClF}_2\text{O}_2\text{NO}_2$.⁹³ This seems to be due to the low probability of the escape of NO_2 molecules from the 'cage' in the solid phase. However, the t^* value determines the limiting concentration of regenerated peroxy macroradicals, $[\text{R}_{\text{in}}\text{O}_2^\bullet]_\infty$ (Fig. 6b)

$$[\text{R}_{\text{in}}\text{O}_2^\bullet]_\infty = \frac{k_{16}}{k_{16} + k_{17}} [\text{R}_{\text{in}}\text{O}_2^\bullet]_0 \exp(-k_{\text{ef}} t^*),$$

where k_{ef} is the effective rate constant for various conversions of peroxy nitrate exposed to NO_2 including those involving alkoxy macroradicals. It was found that $k_{17} < k_{\text{ef}} < 7.6 \times 10^{-5} \text{ s}^{-1}$, i.e., the rate constant of a reaction of the type (17), which can result in degradation of the PTFE macromolecules, does not exceed $\sim 20\%$ of k_{16} .

Unexpected results were obtained in studies of the thermal stability of the reactions products of $\text{R}_{\text{t}}\text{O}_2^\bullet$ with nitrogen dioxide. Heating of samples *in vacuo* at temperatures up to 413 K did not lead to production of free radicals. This can be due to either the fact that no peroxy nitrates are formed in this case or to the fact that the reaction proceeds through a six-membered cyclic transition state and results in the fast formation of stable products.

Thus, if a polymer containing rather stable peroxy radicals (e.g., PTFE) is exposed to high concentrations of nitrogen dioxide for long, the second decomposition route of peroxy nitrate [reaction of the type (17)] can lead to a high degree of degradation of the polymer due to the irreversibility of reaction (18) despite the fact that the corresponding rate constant is five or more times smaller than that typical of the first decomposition route [reaction of the type (16)].

III. The effect of nitric oxide on polymers

Nitric oxide is less reactive than nitrogen dioxide. Currently, it is known with certainty that at room temperature nitric oxide cannot abstract tertiary or allylic hydrogen atoms from organic molecules, since the $\text{H}-\text{NO}$ bond with a strength of $208.6 \pm 2.1 \text{ kJ mol}^{-1}$ is weaker than the $\text{C}-\text{H}$ bonds in organic compounds. Nitric oxide cannot also add to isolated double bonds.⁹⁴⁻⁹⁶ Opinions differ widely as to the ability of NO to react with low-molecular-mass dienes and polyenes. It is known that NO can add to substituted *o*-quinodimethane, phorone and β -carotene to produce free radicals.⁹⁷⁻⁹⁹ It is also believed that the reactions of NO with dienes are actually initiated by admixtures of NO_2 .⁹⁶ In any case, it is of interest to study the regularities of the reaction of nitric oxide with the ageing products of polymers, e.g., hydroperoxides.^{100,101} In addition, NO readily reacts with free radicals to give nitroso compounds, which are efficient spin traps for the free radicals. Analysis of the kinetic curves of the formation and the structures of nitrogen-containing radicals which are stabilised in this case makes it possible to draw conclusions on the mechanisms of free-radical processes in the polymers.

1. Photolysis and radiolysis of poly(methyl methacrylate) and cellulose triacetate in the presence of nitric oxide

Photolysis of PMMA exposed to NO leads to the formation of stable nitrogen-containing radicals. The structures of the radicals formed depend on the temperature and the wavelength of the photolysing light.¹⁰² For instance, acylalkylnitroxyl radicals, $\text{R}^1\text{N}(\text{O}^\bullet)\text{C}(=\text{O})\text{OR}^2$, are produced upon photolysis of PMMA by unfiltered light of a mercury lamp at 298 K. In solid PMMA, they exhibit an anisotropic triplet ESR spectrum with $A_{\parallel}^{\text{N}} = 2.1 \pm 0.1 \text{ mT}$ and $g_{\parallel} = 2.0027$ (Fig. 7a). In a solution of the polymer, the parameters of the ESR spectrum of these radicals are $a^{\text{N}} = 0.8 \pm 0.1 \text{ mT}$ and $g_{\parallel} = 2.0065$. Not only acylalkyl, but also dialkylnitroxyl radicals, $\text{RN}(\text{O}^\bullet)\text{R}$, are produced in the samples photolysed at 383 K. The latter exhibit the ESR spectra

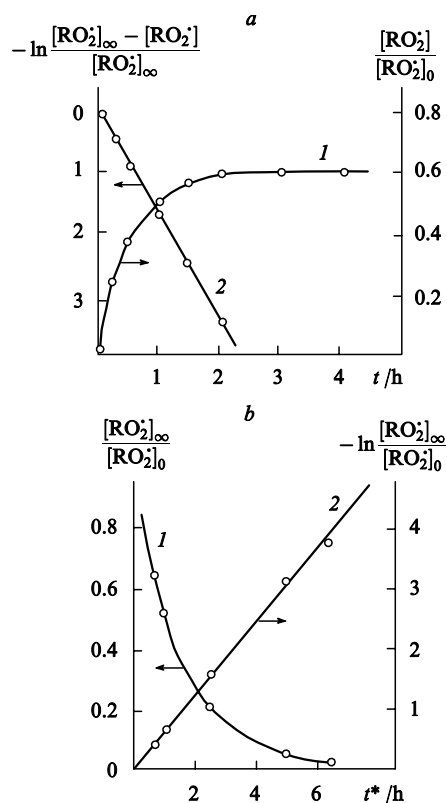
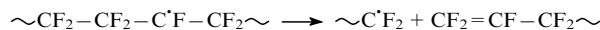
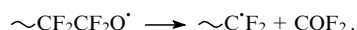
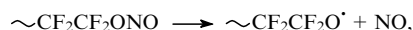
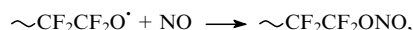
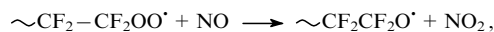


Figure 6. Kinetic curve of regeneration of $\text{R}_{\text{in}}\text{O}_2^\bullet$ radicals after exposure of PTFE to NO_2 ($2.8 \times 10^{-3} \text{ mol litre}^{-1}$) for 1.5 h (a) and the limiting degree of regeneration of $(\text{R}_{\text{in}}\text{O}_2^\bullet)_\infty$ radicals as a function of the time of preliminary exposure of sample t^* to NO_2 ($7 \times 10^{-3} \text{ mol litre}^{-1}$) (b). Kinetic curve (1) and semilogarithmic transformation of curve 1 (2).

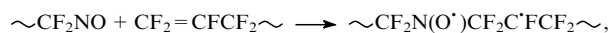
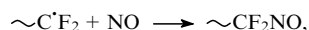
the case of γ -radiolysis of PTFE in oxygen-containing atmosphere, a certain fraction of internal alkyl macroradicals has no time to be oxidised and undergoes decomposition accompanied by scission of the main chain of the polymer.



The terminal alkyl groups are oxidised into terminal peroxide groups so that the neighbouring terminal peroxy macroradicals and terminal double bonds are stabilised in the polymer. After exposure of such samples to NO, the peroxy radicals can be converted as follows:



Terminal alkyl macroradicals recombine with NO to produce terminal nitroso groups neighbouring to the terminal double bonds, which interact with terminal nitrosyl fragments to generate nitroxyl macroradicals



It was found¹⁰⁷ that low-molecular-mass perfluoroalkenes of different structures as well as hydrogen- or fluorine-containing nitroso compounds can enter in these reactions. Similar radicals were also produced in the copolymer of tetrafluoroethylene with hexafluoropropylene.¹⁰⁶ This copolymer was used to generate yet another type of radicals, namely, $\sim\text{CF}_2\text{N}(\text{O}')\text{CF}_3$, with an ESR spectrum consisting of eight HFS components split by 0.88 ± 0.02 mT and $g = 2.0067$. These parameters nearly coincide with the corresponding values for low-molecular-mass perfluoro-nitroxyl radicals of a similar structure in the liquid phase.¹⁰⁷ The pattern of the ESR spectrum of the internal nitroxyl macroradical is due to partial averaging of the anisotropy of HFS and g -factor owing to fast rotation of the nitroxyl fragment about the long axis of the macromolecule. The mobility of the radical fragment in terminal nitroxyl radical is much higher, which in fact is responsible for a complete averaging of the anisotropy of the hyperfine interaction and g -tensors in its ESR spectrum.

Thus, thermally stable spin-labelled macromolecules are generated in the bulk of the samples as a result of post-radiation, free-radical transformations in fluorinated polymers exposed to NO. Their concentration is sufficiently high to allow the ESR studies on molecular dynamics in polymers. The advantage of this method for the introduction of a spin label is that the free-radical (nitroxyl) group can be introduced into various chain fragments, which allows one to obtain optimum information on the macromolecular dynamics.

3. Interaction of polypropylene hydroperoxides with nitric oxide

Polymeric hydroperoxides are reactive intermediates in the oxidative degradation of polymers. Investigations of the reactions of nitrogen oxides with these species furnishes insights into the mechanisms of the effect of air pollutant gases on the stabilities of polymeric materials. For instance, autoaccelerated degradation of PS macromolecules subject to the combined action of NO₂, air and UV radiation was associated with the NO-induced decomposition of hydroperoxides.⁴⁷ It is believed (see, *e.g.*, Refs 100 and 108) that the process begins with the reaction

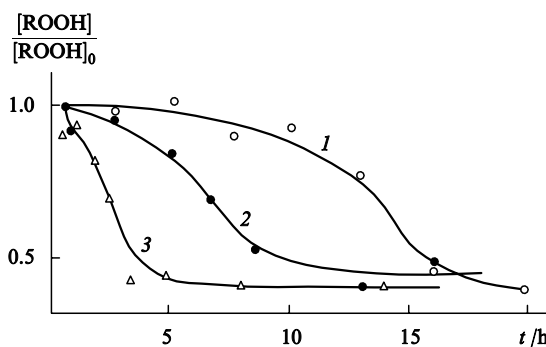
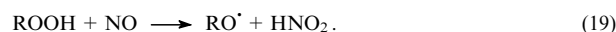


Figure 9. Kinetic curves of consumption of PP hydroperoxides at NO concentrations (in the gas phase) of 1.6×10^{-3} (1), 3.2×10^{-3} (2) and 4.1×10^{-2} mol litre⁻¹ (3).

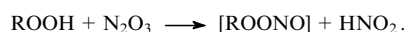
It was also assumed (see Ref. 101) that the reaction proceeds to give the peroxy radicals.



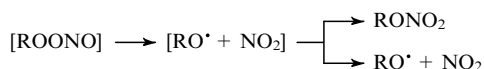
At high concentrations of hydroperoxides, NO-induced decomposition of their dimers was postulated for the liquid phase.¹⁰⁸



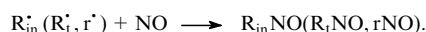
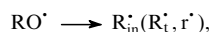
The decomposition kinetics of PP-derived hydroperoxides at 298 K and different NO pressures has been studied in detail.¹⁰⁹ The kinetic curves for decomposition of hydroperoxides are shown in Fig. 9. As can be seen, the rate of hydroperoxide consumption is initially low and then increases substantially. Reactions (19)–(21) cannot provide an explanation for this type of reaction kinetics. Using ESR spectroscopy, it was found that the decomposition of hydroperoxides is accompanied by accumulation of dialkylnitroxyl macroradicals and that the induction period is long. The duration of the induction periods for the decomposition of hydroperoxides and the formation of nitroxyl macroradicals increases as the concentration of nitric oxide in the gas phase decreases and is dependent on the presence of trace amounts of impurities (in particular, NO₂) at a given NO concentration. It was concluded that the primary step in the decomposition of hydroperoxide is initiated by N₂O₃ rather than NO.



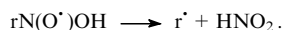
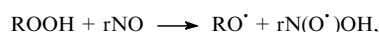
This reaction results in a thermally unstable peroxy nitrite, which can either undergo a fast 'intracage' conversion into nitrate



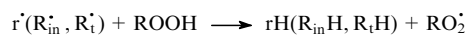
or decompose into alkoxy macroradical and nitrogen dioxide, which then pass in the bulk of the sample. In turn, the alkoxy radicals can either decompose or enter into substitution reaction, thus producing internal (R'_{in}) and terminal (R'_{t}) alkyl macroradicals and low-molecular-mass alkyl radicals r' (see Ref. 100). These radicals react with NO to give nitroso compounds.



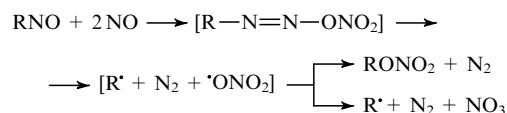
Acceleration of peroxide decomposition can be associated with the reactions which involve nitroso compounds¹¹⁰



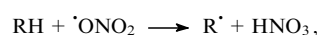
Alkyl radicals formed in the system can initiate decomposition of hydroperoxides.



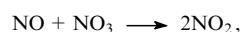
Yet another process which can be responsible for the increase in the hydroperoxide decomposition rate is disproportionation of NO into N₂ and NO₃ in the reactions with the nitroso compounds.⁹⁴



The ONO₂ radical is a highly reactive species (the O₂NO—H binding energy is 423 kJ mol⁻¹, see Ref. 111), which can abstract hydrogen atoms from the PP macromolecules, thus increasing the concentration of free radicals in the polymer



and also reacts with NO



which results in an increase in the concentration of nitrogen dioxide.

Thus, taking PP as an example, it was found that decomposition of hydroperoxides in an atmosphere of NO is initiated by higher nitrogen oxides and proceeds by an autocatalytic mechanism.

In an atmosphere polluted with nitrogen oxides, the primary step of the decomposition of hydroperoxides can be their nitrosation by the dimeric form of nitrogen dioxide, the concentration of which is much higher than that of nitrous anhydride N₂O₃. On account of the great excess of oxygen compared to nitrogen oxides, the probability of the formation of nitroso compounds, which play the key role in the development of autoaccelerated reaction under the conditions used by Gaponova and Pariiskii,¹⁰⁹ must be rather low in a polluted atmosphere due to the oxidation of alkyl radicals into peroxy radicals. Investigation of the ROOH—NO system showed¹⁰⁹ that the results obtained under conditions of accelerated tests must be used with great caution when assessing the stability of polymers in atmosphere polluted with nitrogen oxides.

IV. Conclusion

The results summarised in this review show that nitrogen dioxide, which is an inorganic free radical of moderate reactivity, can perform some functions in the ageing of polymers in polluted atmosphere. On the one hand, at ambient temperatures it can abstract labile hydrogen atoms (tertiary hydrogen atoms in PS and polyvinylpyrrolidone and allylic hydrogen atoms in the polymers containing carbon—carbon double bonds in the main chain) and add to the double bonds of macromolecules, thus generating free radicals and, hence, initiating free-radical ageing processes in the system. At elevated temperatures ($T \geq 373$ K), NO₂ also reacts with stronger C—H bonds, e.g., in the CH₂ groups of polymers. On the other hand, it can react with alkyl, alkoxyl and peroxy macroradicals generated in the reactions, thus inhibiting free-radical transformations of polymers and resulting in valence-saturated products of different thermal stabilities.

The dimer of nitrogen dioxide, N₂O₄, is an efficient nitrosating agent and its reactions are responsible for the ageing of the polymers containing amide groups (polyamides, polyurethanes and polyamidoimides). Free-radical reactions initiated by NO₂ are accompanied by production of stable nitrogen-containing radicals. Analysis of their structures and kinetics of formation provides additional information on the free-radical stages of complex processes of nitration of polymers under various conditions.

Nitric oxide, NO, is also a paramagnetic molecule, which is much less reactive than nitrogen dioxide. At ambient temperatures, it cannot abstract even the most mobile (labile) hydrogen atoms from the molecules of organic compounds or add to isolated double bonds to produce free radicals. In addition, it is an efficient acceptor of free radicals which can inhibit free-radical chain reactions. Nitroso compounds formed in the reactions with alkyl radicals are efficient spin traps and can in turn inhibit free-radical processes in polymers. However, at high NO pressures their reactions with nitroso compounds lead to disproportionation of NO into N₂ and ONO₂, which is a reactive radical capable of initiating free-radical processes in polymers. This reaction seems to be the stage responsible for autoaccelerated decomposition of hydroperoxides in an atmosphere of nitric oxide.

Free radicals in solid polymers can be generated by photolysis, γ -radiolysis, thermal decomposition of initiators etc. Free-radical processes in solid polymers carried out in an atmosphere of NO are accompanied by production of nitrogen-containing macroradicals of different structures. Analysis of their structures and kinetics of formation allows one to obtain additional information on the mechanisms of the above-mentioned processes. Performing free-radical reactions in chemically inert, insoluble polymers [e.g., poly(perfluoroalkenes)] in an atmosphere of nitric oxide makes it possible to prepare spin-labelled macromolecules with either internal or terminal NO[•] groups. These spin labels perturb the polymer chain dynamics to the smallest extent and are therefore the most appropriate for using in the ESR studies.

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^c — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*

^d — *Kinet. Catal. (Engl. Transl.)*

^e — *Chem. Phys. Rep. (Engl. Transl.)*

Tandem transformations initiated and determined by the Michael reaction

E V Gorobets, M S Miftakhov, F A Valeev

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Abstract. Data on tandem transformations initiated by the Michael reaction published over the last five years are analysed, systematised and generalised. The bibliography includes 86 references.

I. Introduction

Syntheses of polyfunctional organic compounds with complex structures from simpler compounds by tandem one-pot transformations were described in a series of reviews (see, for example, Refs 1–6). Tandem transformations are multistep transformations in which each subsequent step is strictly determined by the preceding one and occurs under the same reaction conditions. The advantage of these transformations is the formation of several bonds and complication of the structure of the compound in one step, which is generally accompanied by the high stereoselectivity of the reaction. Minimisation of waste products, a decrease in the amount of required solvents, reagents and adsorbents, reduction in the energy and a decrease in the number of laboratory operations provide the economic and ecological feasibility of this type of processes.

According to the mechanism of the first step, tandem conversions are divided into cationic, anionic, radical, pericyclic, photochemical and transition-metal-induced processes. The terms 'tandem', 'cascade' and 'domino' reactions are used as synonyms.

Most tandem transformations proceed through the formation of an anionic intermediate. This first step governs the subsequent transformations. Most often, deprotonation of the CH group of

the substrate occurs giving rise to a carbanion followed by its reaction with an electrophile to form a new anionic intermediate. This anion can attack another electrophilic centre, *etc.* The sequence is completed with trapping of an electrophile (for example, H^+) or elimination of the leaving group X^- .

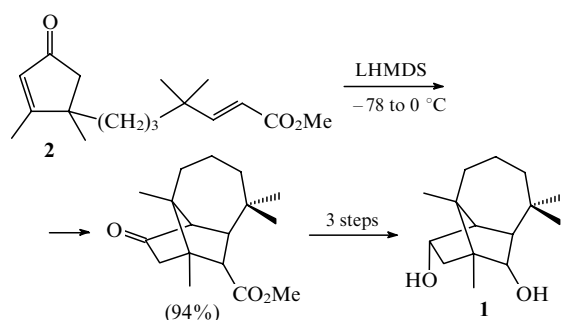
In many cases, anionic transformations are either initiated or governed by the Michael reaction. In the present review, most attention is given to this type of transformation studied in recent years.[†]

II. A tandem Michael reaction

One of the approaches which is most popular for the formation of C–C bonds is based on the Michael reaction involving compounds containing an activated methylene group and α,β -unsaturated esters or ketones. A combination of two consecutive Michael addition reactions has considerable promise for the efficient construction of cyclic and polycyclic compounds because the second addition reaction often results in ring closure. This type of transformation is named the Michael Ring Closure (MIRC) or the Michael-Michael Ring Closure (MIMIRC).² Of all tandem transformations, a combination of two Michael reactions has been described in most detail. The examples considered below clearly demonstrate the importance of this approach in synthetic organic chemistry.

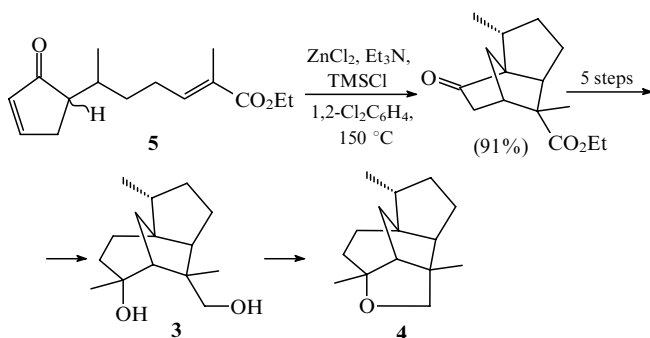
In studies of intramolecular double Michael addition reactions, a series of polycyclic structures were prepared⁷ which served as the basis for the total synthesis of some natural compounds. The total synthesis of a sesquiterpenoid fungicide ($\pm$)-culmorin (**1**) was developed.⁸ The tricyclo[6.3.0.0^{3,9}]undecan-10-one skeleton of **1** was constructed in one step by intramolecular cyclisation of 4-substituted cyclopent-2-enone **2** according to a scheme of double conjugate addition.

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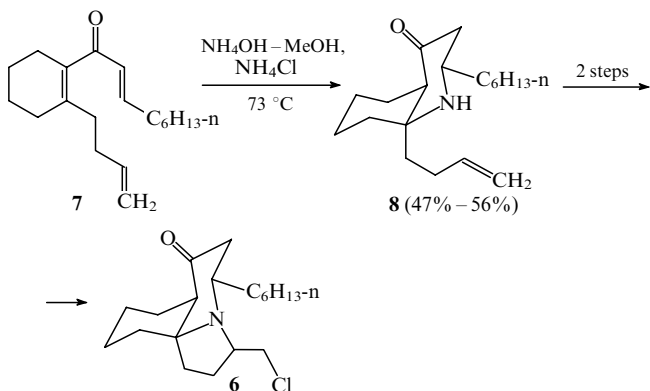
LHMDS is lithium hexamethyldisilazide.

The same strategy was used for the preparation of sesquiterpenoids ($\pm$)-8,14-cedranediol (**3**) and ($\pm$)-8,14-cedrane oxide (**4**) based on 5-substituted cyclopent-2-enone **5**.^{9, 10}

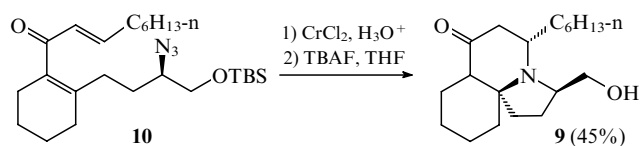


TMSCl is trimethylsilyl chloride.

The total synthesis of alkaloid cylindricine A (**6**) of animal origin, which was first isolated from ascidia in 1993, was performed.¹¹ The Michael addition of ammonia to the conjugated diene system of the ketone **7** afforded the key synthon, *viz.*, perhydroquinolinone **8**. Its subsequent reaction with *N*-chlorosuccinimide and radical cyclisation gave rise to a 55 : 45 mixture of cylindricine A (**6**) and its epimer, which could be readily separated.



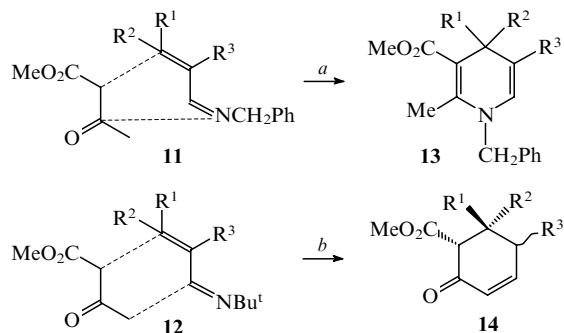
The total synthesis of alkaloid cylindricine C (**9**) related to compound **6** was performed in two steps¹² starting from the azide **10**. Selective reduction of the azide in the presence of the diene system was carried out with the use of CrCl_2 . The resulting amine entered into the highly convergent and efficient double Michael addition reaction.



TBS is the *tert*-butyldimethylsilyl group, TBAF is tetrabutylammonium fluoride.

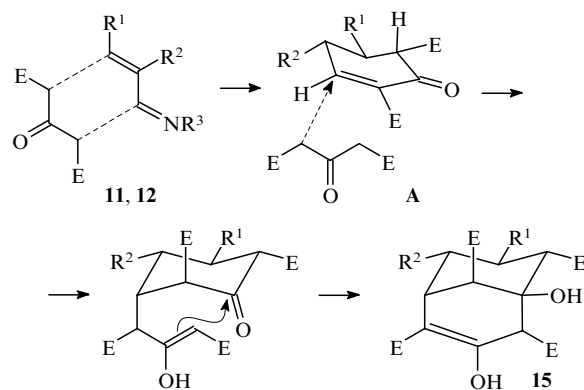
The synthetic potential of enamines in a two-step process involving the Michael addition followed by cyclisation has been examined.¹³ Readily accessible 1-aza-1,3-butadienes (enamines) **11** and **12** reacted with methyl acetoacetate and acetylacetone in the presence of catalytic amounts of LiI to form unsymmetrically substituted 1,4-dihydropyridines **13** or cyclohexenone derivatives **14**.

The reaction pathway depends on the structure of the enamine used. The reaction of methyl acetoacetate with *N*-benzylenamines of type **11** gives rise to 1,4-dihydropyridine derivative **13**. If the benzyl group in the acceptor is replaced by the *tert*-butyl group (compound **12**), the reaction follows another pathway to form the cyclohexenone derivative **14**. In these reactions, either two (path *a*) or three (path *b*) carbon atoms of the 1,3-dicarbonyl compound are involved in the formation of the six-membered ring.



$\text{R}^1 = \text{Alk}$, Ar ; $\text{R}^2, \text{R}^3 = \text{H}$, Alk .

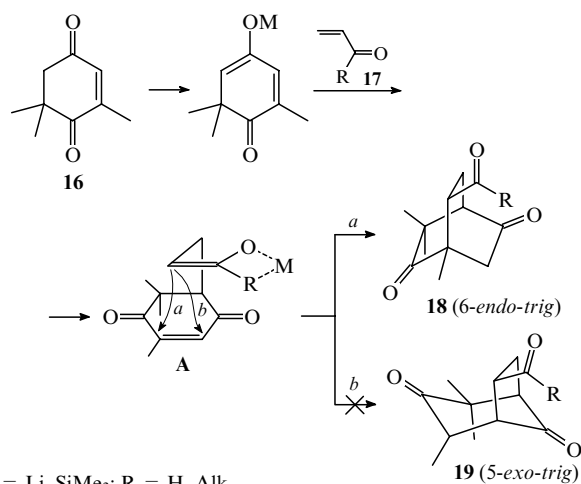
This divergence was not observed in the reactions of enamines **11** and **12** with dimethyl 3-oxoglutarate. Both enamines formed derivatives of bicyclo[3.3.1]nonan-3-one **15**.



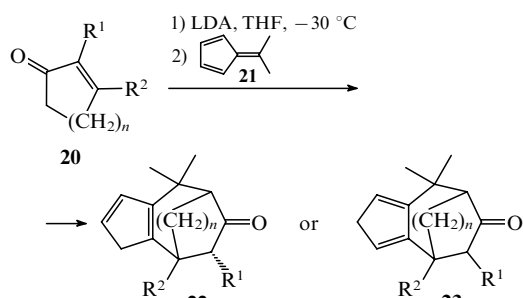
$\text{E} = \text{CO}_2\text{Me}$; $\text{R}^1, \text{R}^2 = \text{H}$, Alk , Ar ; $\text{R}^3 = \text{CH}_2\text{Ph}$ (**11**), Bu^t (**12**).

This result indicates that two molecules of the oxo diester are involved in the reaction. When the diester and enamine were taken in a ratio of 2 : 1, the product **15** was obtained in higher yield. The possible mechanism of transformation involves the formation of the intermediate **A**, which enters into the second Michael reaction followed by cyclisation.

The double Michael addition makes it possible to construct the bicyclo[2.2.2]octane skeleton of many natural compounds based on oxophorone (**16**) and its derivatives.¹⁴ The reactions of oxophorone enolates with α,β -unsaturated carbonyl compounds **17** gave rise to the intermediate **A**, which underwent 6-*endo-trig* cyclisation following the path *a* to form the only product **18**. The isomer **19**, which could be formed in the case of the path *b*, was not detected.

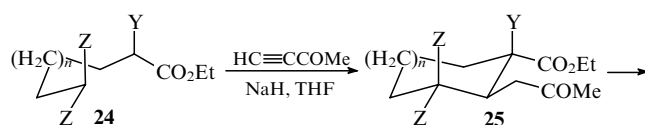


The double conjugate addition of enones **20** to fulvene (**21**) offers a convenient approach to tricyclo[5.3.0.*n*^{2,5}]alkane systems.¹⁵ The dienolate anion generated from enone enters into the Michael reaction with fulvene to give an anionic intermediate. The latter undergoes cyclisation as a result of the intramolecular Michael reaction giving rise to tricyclic ketone **22** or **23** with high stereoselectivity. The reaction is particularly efficient with the use of cyclopentenone as the Michael acceptor. In the latter case, tricycloalkanes are obtained in 75%–96% yields.

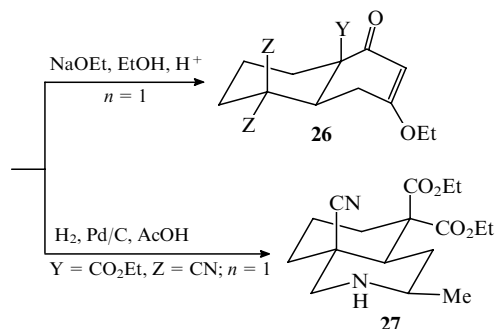


R¹, **R**² = H, Alk; *n* = 1–3; LDA is lithium diisopropylamide.

The new method for the construction of polyfunctional cyclic compounds containing several substituents developed by Grossman *et al.*^{16–19} is based on the use of the double Michael reaction of carboxylates **24** with but-3-yn-2-one.



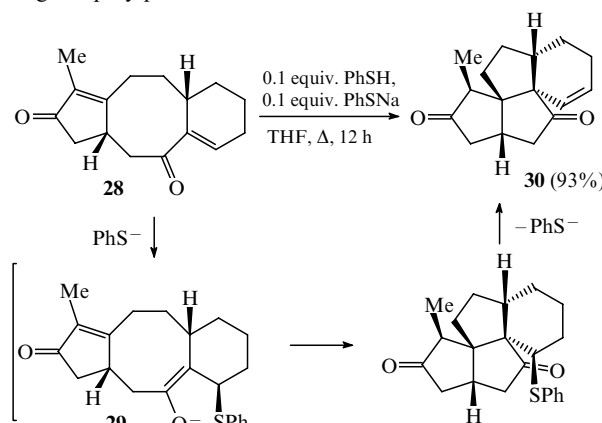
Y, **Z** = CN, CO₂Et; *n* = 0, 1.



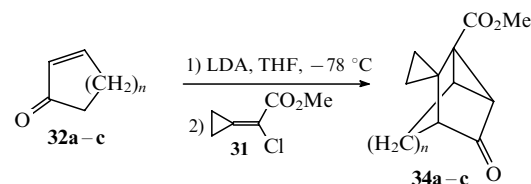
Cyclic products **25** are convenient starting compounds for the synthesis of biologically active polycyclic compounds. In particular, the Dieckmann reaction and intramolecular reductive ami-

nation of these compounds afforded *trans*-decalin **26** and *trans*-perhydroisoquinoline **27**, respectively. Three new C–C or C–N bonds, the ring system of bicyclo[4.4.0]decane and up to four new stereocentres can be constructed starting from two readily accessible acyclic compounds.

Tandem reactions giving rise to angular polyquinanes were reported.²⁰ The derivative of squaric acids, *viz.*, *cis*-13-methyltricyclo[10.3.0.0^{4,9}]pentadeca-4(5),12(13)-diene-3,14-dione (**28**), was involved in intramolecular cyclisation initiated by PhS[–]. Enolate **29** formed in the first intermolecular Michael reaction underwent intramolecular transannular cyclisation in the second step to give the angular polyquinane **30**.

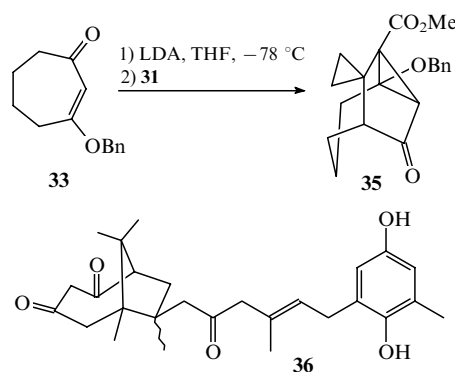


The Michael reactions of methyl (chloro)cyclopropylideneacetate (**31**) with cyclic dienolates formed from enones **32** and **33** were studied.²¹ These reactions gave rise to tricyclic adducts **34** and **35**, respectively. It was proposed that the compound **35** can be used as an intermediate in the synthesis of sea diterpenoids, *viz.*, mediterraneols A and B (**36**).

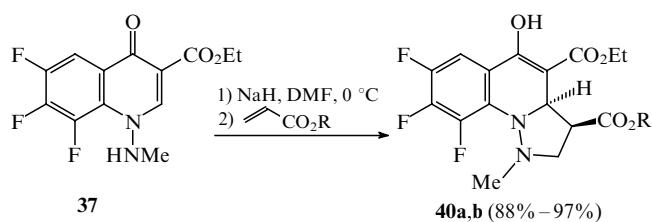


n = 5 (**a**), 6 (**b**), 7 (**c**).

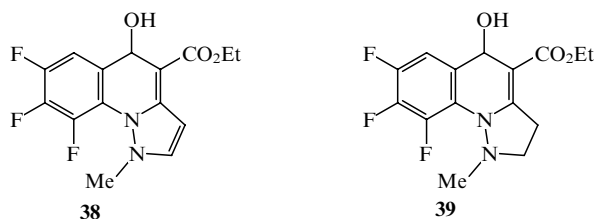
Compound 34	Yield (%)
a	40
b	34
c	78



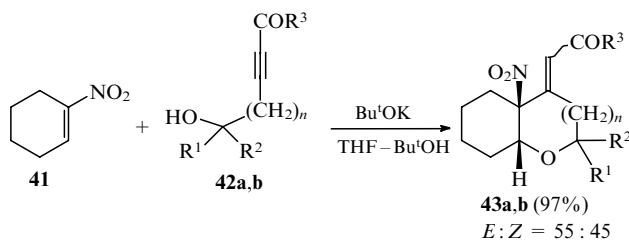
The methodology of tandem 1,4-inter- and intramolecular addition reactions has been used for the preparation of pyrazolo[1,5-*a*]quinoline ring systems **38** and **39** inhibiting DNA synthesis in bacteria starting from the quinolone **37**.²² The key tricyclic synthons **40a,b** were synthesised by the reactions of the quinolone **37** with different acrylates.



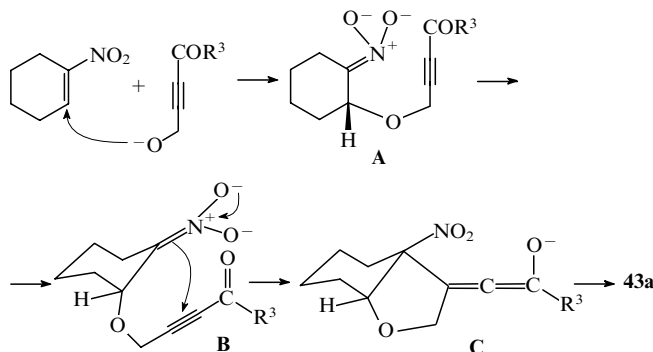
R = Me (a), Bu^t (b).



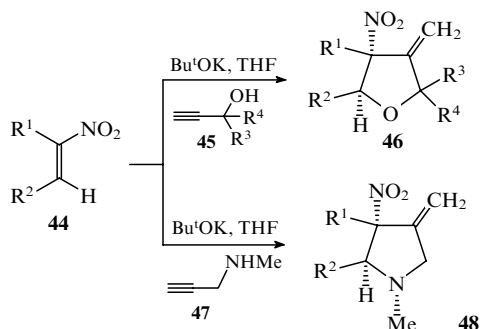
The double Michael reactions of 1-nitrocyclohexene (**41**) with ynols **42a,b** afforded nitrooctahydrobenzofurans (**43a**) and -pyrans (**43b**), respectively.²³ The possible reaction mechanism involves the addition of the alcohols **42a,b** at the double bond of the cycloalkene **41** and intramolecular cyclisation of the resulting anion **A** via the transition state **B** to give the anionic intermediate **C** containing *cis*-fused rings. Subsequent protonation of the anion **C** affords a mixture of the *E*- and *Z*-isomers **43a,b**.



n = 0 (a), 1 (b); R¹, R² = H, Alk; R³ = OAlk, NMe₂.



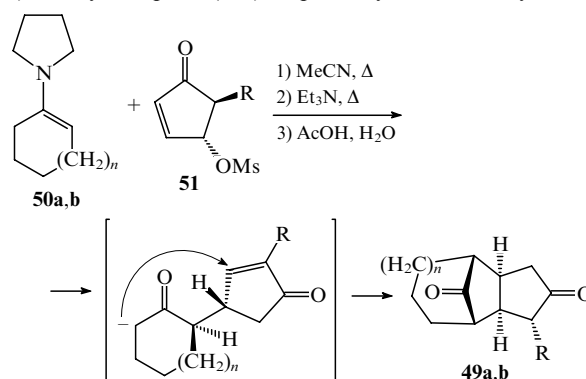
The use of terminal alkynes enables one to change the order in which the reagents enter into the reaction. In this case also, the reaction results in a five-membered heterocyclic compound.²⁴ Thus the reaction of acyclic nitroalkene **44** with the ynol **45**



R¹ = Alk; R² = Alk, Ar; R³, R⁴ = H, Alk.

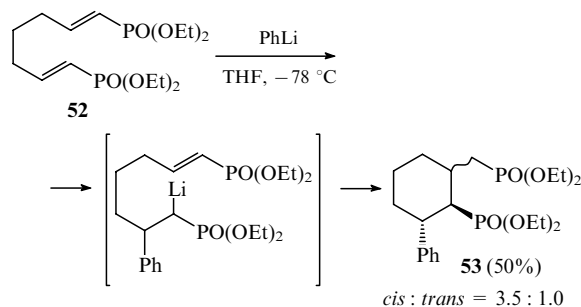
afforded tetrahydrofuran derivative **46**. The aza-Michael addition of *N*-methylprop-2-ynylamine (**47**) to nitroalkenes **44** proceeded regio- and stereoselectively to form 3-methylenepyrrolidines **48**.

A new procedure for the stereoselective preparation of tricyclo[5.3.1.0^{2,6}]undecane-4,11-diones (**49a**) and tricyclo[5.4.1.0^{2,6}]dodecane-4,12-diones (**49b**) is based on the inter- and intramolecular Michael reactions of 1-pyrrolidinocyclohexene (**50a**) and -cycloheptene (**50b**), respectively, with the mesylate **51**.²⁵

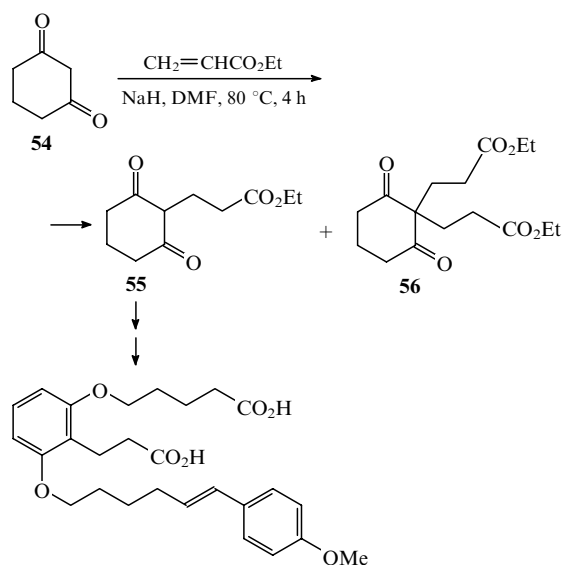


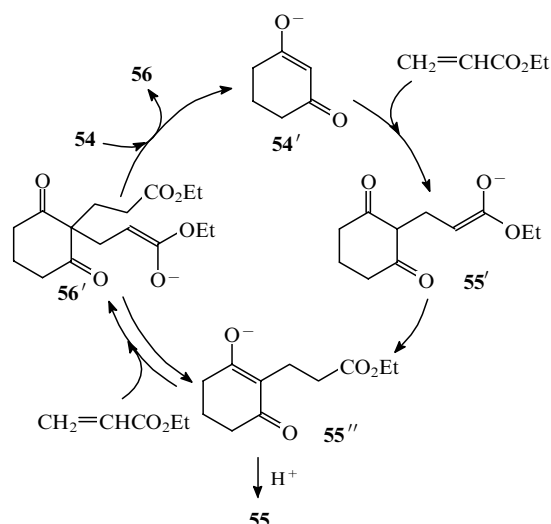
R = Alk, Ar; *n* = 1 (a), 2 (b); Ms is mesyl.

Organolithium compounds initiate Michael cyclisation of α,β,ψ,ω-unsaturated bisphosphonates **52**.²⁶ Thus the addition of PhLi to a solution of tetraester **52** afforded cyclic bisphosphonate **53**, which is a product of the tandem Michael reaction.



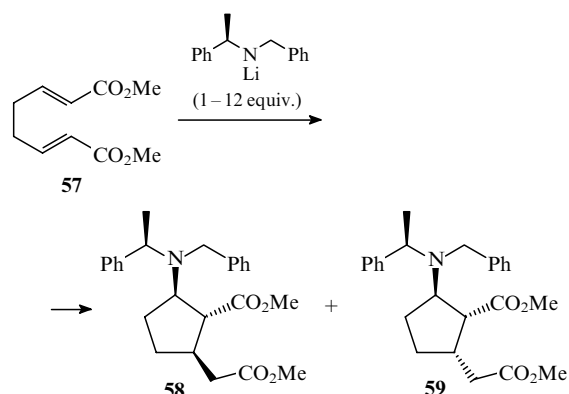
The reaction of cyclohexane-1,3-dione (**54**) with ethyl acrylate proceeded as an intermolecular double Michael addition.²⁷





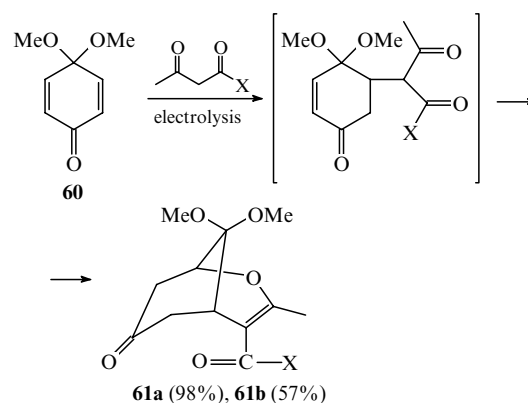
In the presence of catalytic amounts of a base, the reaction gave rise to a mixture of two products, *viz.*, **55** and **56**, in a ratio of 3 : 1. The reaction in the presence of an equimolar amount of a base afforded only the monoaddition product **55**. The observed difference can be explained as follows. An appropriate amount of the enolate anion **54'** is generated under the action of catalytic amounts of a base. The Michael reaction of this anion with ethyl acrylate yields the anion **55'** whose intramolecular isomerisation gives rise to the anion **55''**. The latter either undergoes protonation to form the product **55** or enters into the second Michael reaction. The enolate anion **56'** abstracts the labile proton from the diketone **54** yielding the anion **54'** and the diester **56**. As a result, a mixture of the products **55** and **56** is obtained. In the presence of one equivalent of a base, the enolate anion **54'** is formed in quantitative yield. The Michael reaction affords the anion **55'**, which undergoes intramolecular deprotonation–protonation to give the anion **55''** and then exclusively the monoaddition product **55**.

Esters of $\alpha,\beta,\alpha',\beta'$ -dienedioic acids can serve as potential substrates for anionotropic tandem transformations. The intermediate enolate which is generated in the first step of intermolecular conjugate addition of the nucleophile attacks the second α,β -unsaturated ester group according to an intramolecular mechanism. The use of a chiral nucleophile in these tandem conversions allows the preparation of optically active adducts. Thus the reaction of homochiral lithium [(1*R*)-methylbenzyl]benzylamide with dimethyl octa-2,6-dienedioate (**57**) gave rise to chiral cyclopentane derivative **58**, the configurations of the C(1) and C(2) atoms being completely controlled and the configuration of the C(5) atom being controlled to a large degree [the content of the C(5)-epimer **59** was < 5%].²⁸



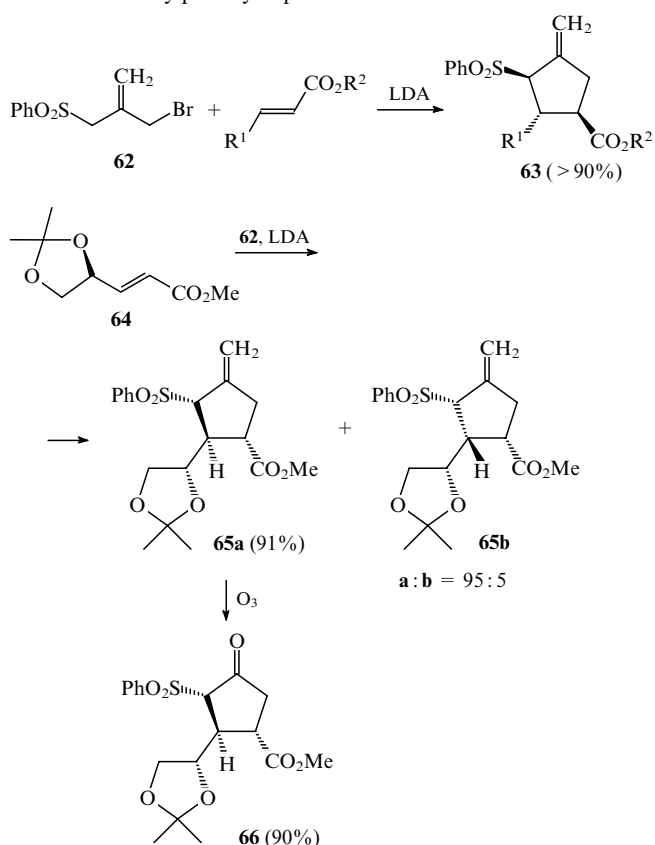
The reaction of 4,4-dimethoxycyclohexa-2,5-dienone (**60**) with ethyl acetoacetate and acetylacetone proceeded as a tandem

Michael reaction.²⁹ Compounds **61a,b** were formed as a result of successive Michael C- and O-addition.



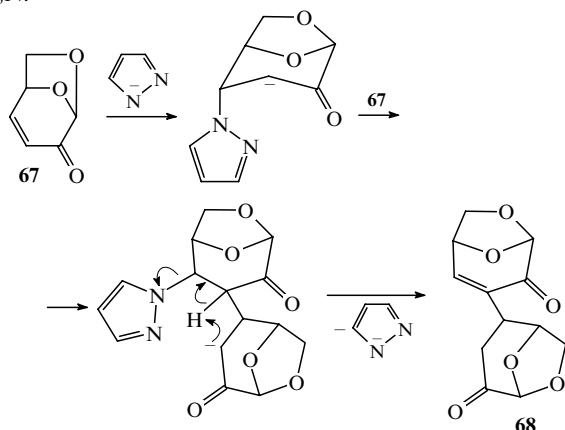
X = OEt (**a**), Me (**b**).

The bifunctional reagent, *viz.*, 2-bromomethyl-3-phenylsulfonylprop-1-ene (**62**), reacts with different electrophilic alkenes to give [3 + 2]-cycloadducts.³⁰ The use of acyclic (*E*)-enoates in these reactions allows the preparation of stereohomogeneous *trans*, *trans*-trisubstituted methylenecyclopentanones **63** in high yields (90%). The tandem reactions of bromosulfone **62** with α,β -unsaturated esters containing the O atom at the γ position, in particular, with (4*S*)-enoate **64**, also proceeded with good facial selectivity. Subsequent ozonolysis of the alkene **65a** gave rise to enantiomerically pure cyclopentanone **66**.

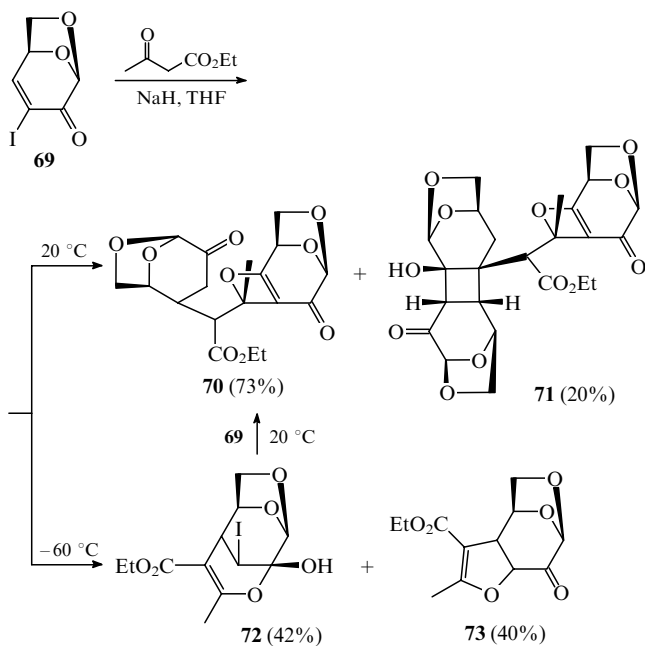


Abundant data on tandem reactions of 1,6-anhydro-3,4-dideoxy- β -D-glycero-hexopyranos-3-en-2-one, the so-called levoglucosenone (**67**), are now available in the literature (see, for example, Refs 31–33). Interesting conversions take place upon treatment of levoglucosenone with pyrazole under conditions of electrolysis. The first stage involves the cathode-initiated addition of pyrazole followed by the selective addition of yet another molecule **67** to the adduct to form the dimer **68** in quantitative yield.³⁴ Previously, the dimer **68** was obtained in low yield (8%)

along with trimers³³ by heating levoglucosenone in aqueous Et₃N.

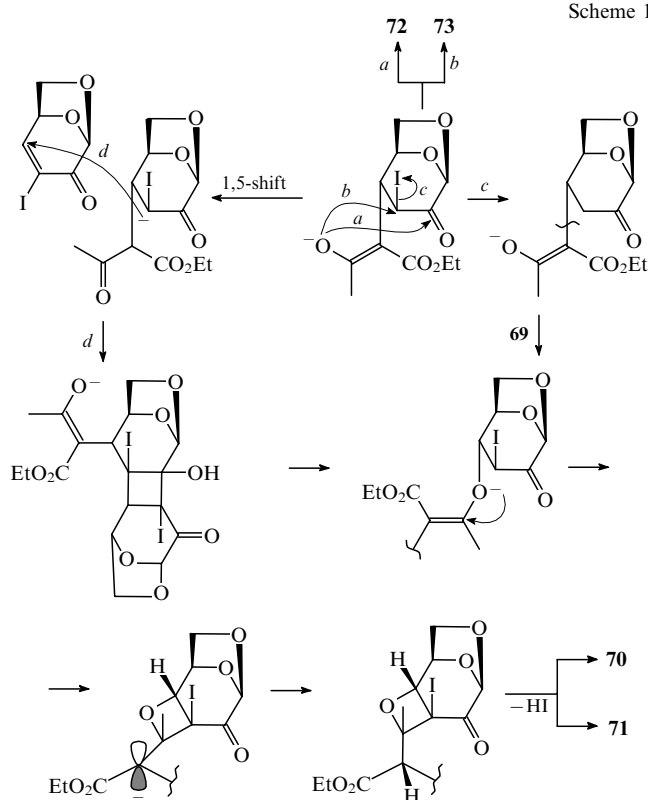
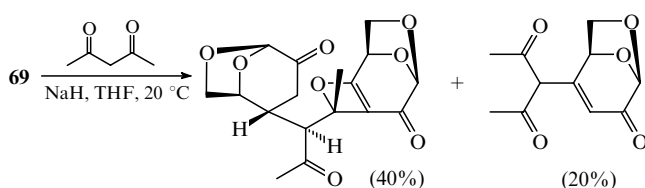


The introduction of the halogen atom at position 3 of levoglucosenone extends the possibilities of its tandem transformations. The effects of the temperature and the reagent ratio on the structure of the product were examined using the reaction of sodium ethyl acetoacetate with 3-iodolevoglucosenone (**69**) as an example.³⁵



The reactions with an excess of the ketone **69** (2 equiv.) at room temperature afforded two products, viz., stable oxetene derivative **70** and polycyclic compound **71** containing the cyclobutane fragment. The reaction of equimolar amounts of the reagents at -60°C gave rise to 1:1 adducts **72** and **73**. It should be noted that the reaction of the compound **72** with 3-iodolevoglucosenone in the presence of NaH yielded the adduct **70**.³⁶ The assumed mechanism of conversions is shown in Scheme 1.

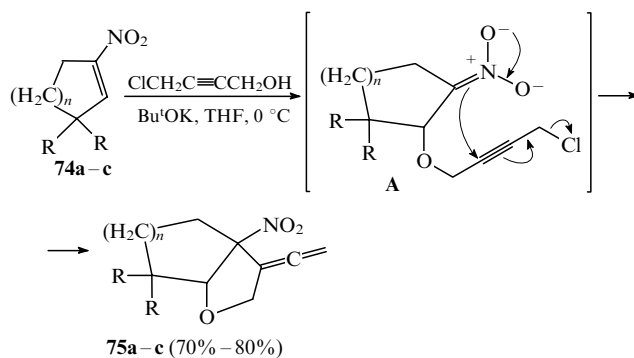
The reaction of yet another representative of CH-acids, viz., acetylacetone, with 3-iodolevoglucosenone (**69**) proceeded analogously.



III. Tandem 'Michael reaction – nucleophilic substitution' sequence

As mentioned above, the addition of a nucleophile to an acceptor gives rise to an anionic intermediate, which can act as a new nucleophile. If the molecule of the latter contains a good leaving group X, the subsequent intramolecular nucleophilic substitution can occur.

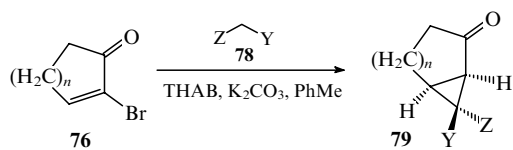
The procedure 'tandem oxa-Michael addition – intramolecular S_N2'-substitution' was used³⁷ for the efficient and stereo-controlled synthesis of poorly studied allenetetrahydrofurans. Nitrocycloalkenes **74a–c** react smoothly with 4-chlorobut-2-yn-1-ol to give bicyclic adducts **75a–c**. The reaction mechanism is analogous to that of the well-studied reactions of nitroalkenes with O-nucleophiles. Initially, the oxa-Michael addition affords the nitronate **A**, which undergoes cyclisation of the S_N2' type to form the allene derivative **75**.



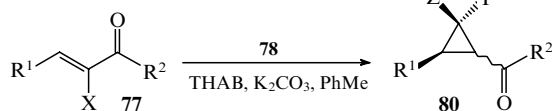
R = H, $n = 1$ (a); R = H, $n = 2$ (b); R–R = OCH₂O, $n = 2$ (c).

A procedure for cyclopropanation of cyclic and acyclic enones is based on the 'intermolecular Michael reaction – intramolecular alkylation' sequence.³⁸ Thus the reactions of readily accessible

α -haloenones **76** and **77** with mild C-nucleophiles **78** gave rise to cyclopropane derivatives **79** and **80**, respectively.

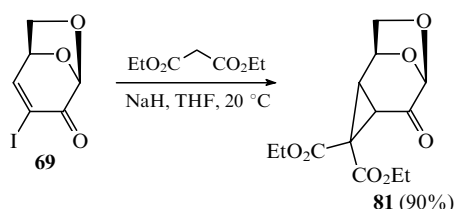


$n = 1, 2$; $Y = \text{CO}_2\text{Alk}, \text{CN}, \text{H}$; $Z = \text{CO}_2\text{Alk}, \text{NO}_2$; THAB is tetrahexylammonium bromide.

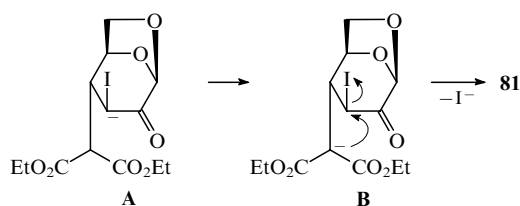


$X = \text{Cl}, \text{Br}$; $R^1, R^2 = \text{Alk}, \text{Ar}$.

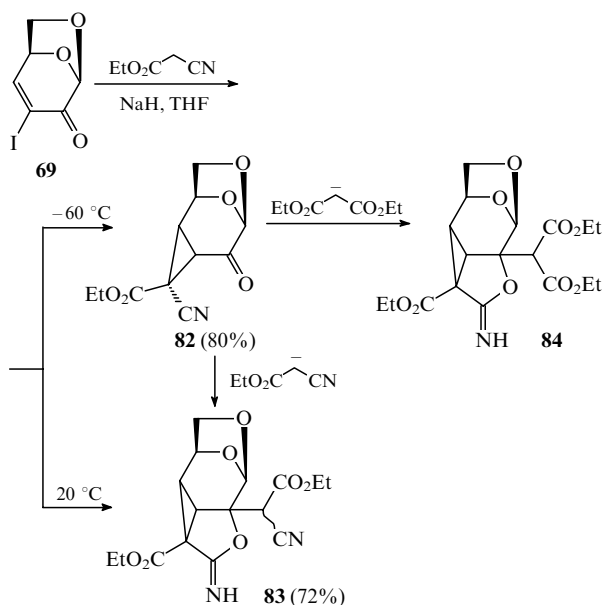
Cyclopropane derivative **81** was synthesised by the reaction of the malonate anion with 3-iodolevoglucosenone (**69**) as an electrophilic component.³⁹



Apparently, a 1,3-shift of electron density occurs in the intermediate carbanion **A** resulting in generation of the more stable carbanion **B**, which eliminates the iodide ion to give the product **81** containing the cyclopropane ring.



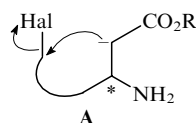
Analogously, 3-iodolevoglucosenone (**69**) reacted with sodium ethyl cyanoacetate at -60°C to give the corresponding cyclopropane **82**.³⁵ However, the reaction of the ketone **69** with ethyl cyanoacetate at 20°C afforded imide **83**, which is the product of the cascade reaction of the cyclopropane **82** with a



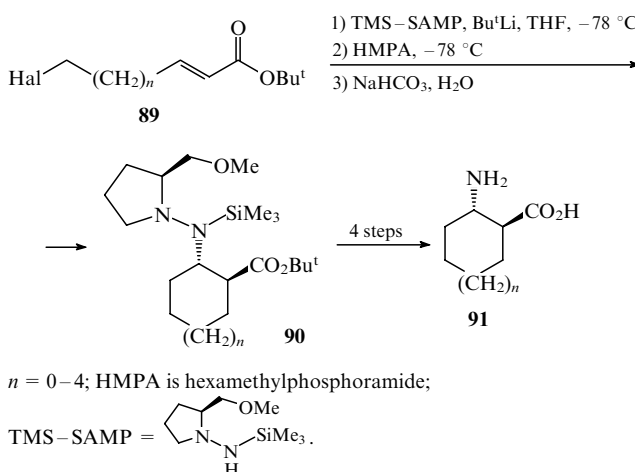
second cyanoacetate anion. This fact was confirmed by the reaction of the individual cyclopropane **82** with sodium ethyl cyanoacetate or the malonate anion at 20°C giving rise to tetracyclic compounds **83** and **84**, respectively.

The classical tandem reaction of polyfunctional substrates, *viz.*, of electrophile **85** and nucleophile **86**, (Scheme 2) has been described.⁴⁰ It appeared that the result of transformations is governed by the order in which the reagents are added. The addition of dimethyl 3-oxoglutarate (**86**) to a suspension of the dibromide **85** (*i.e.*, in the presence of an excess of **85**) and Na_2CO_3 in dry THF afforded substituted benzo[*g*]isochromene **87**. On the contrary, the addition of the dibromide **85** to a suspension of the diester **86** (*i.e.*, in the presence of an excess of **86**) and Na_2CO_3 in THF gave rise to a derivative of cyclopenta[1,3]cyclopropa[1,2-*b*]naphthalene **88**. The observed selectivity can be explained as follows. Alkylation of the β -oxo ester **86** with the highly reactive benzyl-type bromide **85** leads to the intermediate **A**. The latter can react in two different ways. In the presence of an excess of the bromide **85**, the intermediate **A** is subjected to O-alkylation to form the intermediate **B**, which undergoes the intramolecular Michael cyclisation with elimination of HBr to give benzoisochromene **C**. Isomerisation of the double bond in the latter affords the final product **87**. If the reagents are added in the reverse order, the intramolecular Michael reaction takes place and the intermediate **A** is converted into the spiro compound **D**. The latter undergoes smooth cyclisation to form cyclopropane **E** and subsequent alkylation at the activated CH group with the second molecule of the dibromide **85** affords the product **88**.

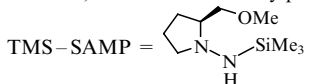
A new strategy for the synthesis of carbocyclic β -amino acids was reported.⁴¹ The conjugate addition of the chiral analogue of ammonia, *viz.*, (*S*)-(-)-1-(trimethylsilylamino)-2-(methoxymethyl)pyrrolidine (TMS-SAMP), to ω -halogen-substituted enoates **89** gave rise to intermediate ester **A**,



which underwent intramolecular cyclisation to give compound **90** with high stereoselectivity. Subsequent removal of the protective trimethylsilyl group, reduction of the N–N bond and hydrolysis of the ester group afforded carbocyclic β -amino acid **91**.

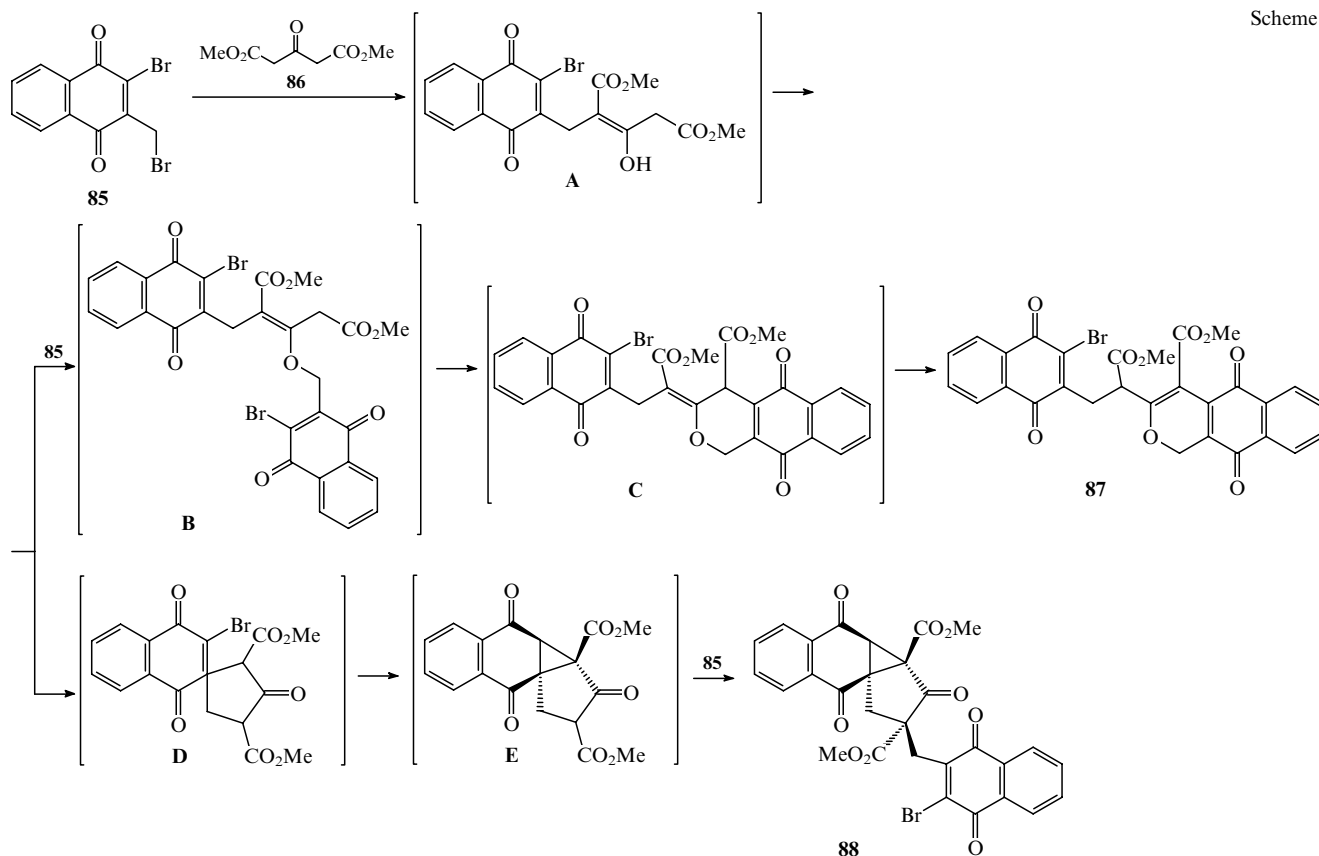


$n = 0-4$; HMPA is hexamethylphosphoramide;

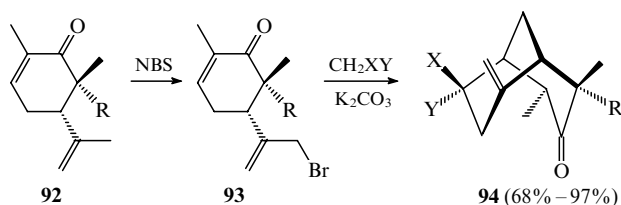


A procedure for the synthesis of chiral bicyclo[3.3.1]nonanes from homologues of carvone (**92**) has been developed.⁴² The reactions of allylic bromides **93** with different CH-acids occur as

Scheme 2



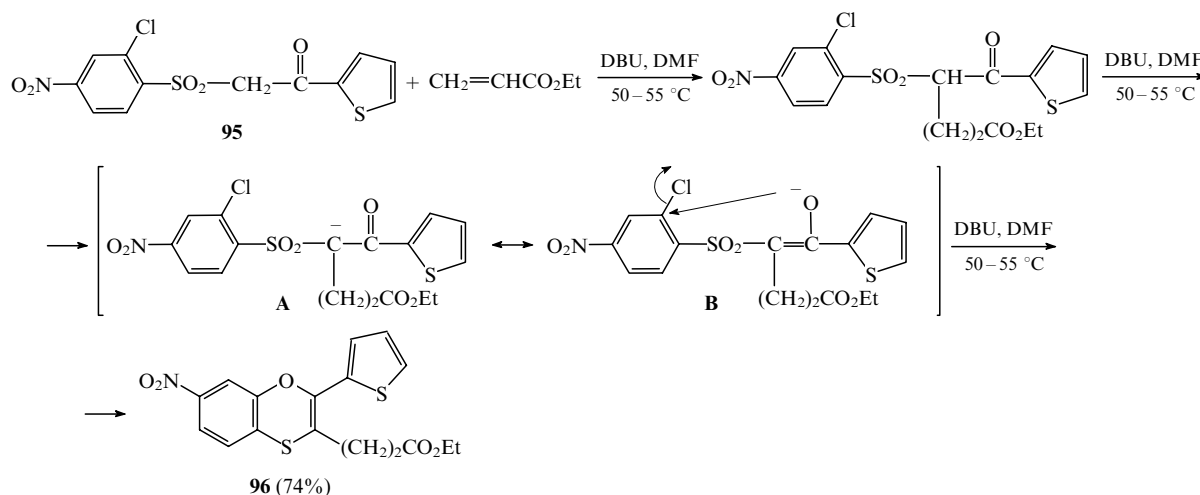
the tandem ‘intermolecular alkylation–intramolecular Michael reaction’ sequence giving rise to bicyclic compounds **94**.



R = H, Me; X, Y = CO_2Alk ; NBS is *N*-bromosuccinimide.

The reaction of 2-(2-chloro-4-nitrophenylsulfonyl)acetylthiophene (**95**) with ethyl acrylate proceeds in a ‘Michael reaction–nucleophilic substitution’ sequence.⁴³ The possible mechanism involves generation of the anions **A** and **B** under basic conditions. The oxygen atom of the anion **B** bearing a negative charge can readily attack the C(2) atom of the benzene ring resulting in intramolecular nucleophilic substitution to form cyclic product **96** (Scheme 3).

Scheme 3

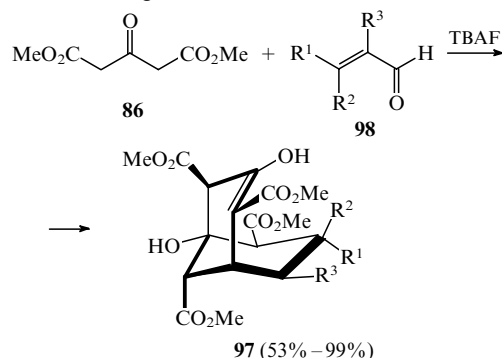


DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene.

IV. Tandem 'Michael reaction – aldol reaction' sequence

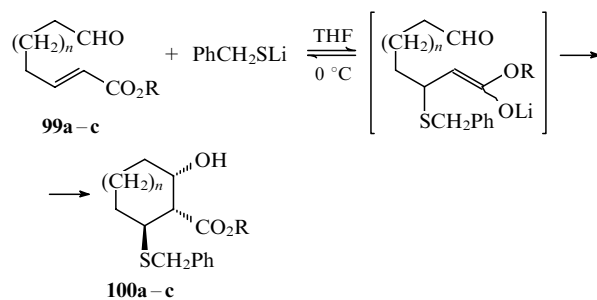
The basic medium required for the Michael reaction favours a subsequent aldol reaction. This type of transformation has been described in the literature in detail.

The short stereospecific synthesis of bicyclo[3.3.1]nonane derivatives (**97**) from acyclic diester **86** and enal **98** was performed by Michael addition followed by intramolecular aldolisation with the use of the reagent ratio **86**:**98** = 2:1.⁴⁴



$R^1, R^2, R^3 = \text{H, Alk, Ar.}$

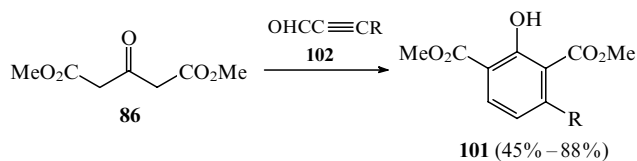
An efficient procedure was developed for the construction of five–seven-membered carbocycles by the tandem 'Michael reaction – aldol cyclisation' sequence based on ω -oxo- α,β -unsaturated esters **99**.⁴⁵ Treatment of the latter with lithium α -toluenethiolates afforded cyclisation products **100** with a good stereoselectivity and in high yields.



Compounds 99 and 100	R	n	Yield of 100 (%)
a	Et	0	96
b	Me	1	95
c	Et	2	33

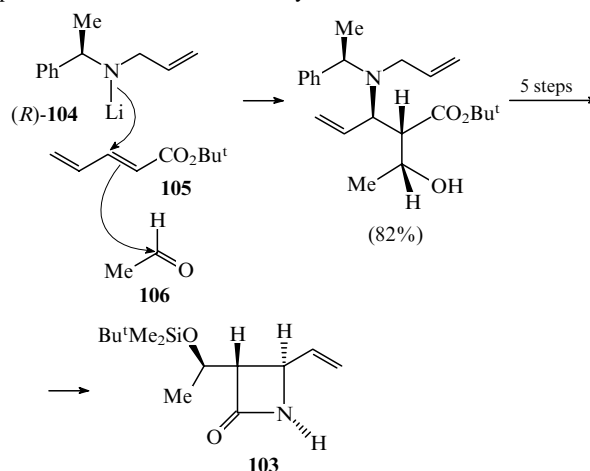
An efficient one-pot procedure was proposed for the construction of trisubstituted phenols **101** starting from prop-2-ynals **102** and the diester **86**.⁴⁶ This tandem process involves the Michael addition followed by aldol cyclisation of the intermediate enolate

anion. The phenols **101** were obtained in high yields. Only the reaction with the use of propynal ($R = \text{H}$) as an acceptor gave the product in low yield (11%), which is attributable to side anionic polymerisation of propynal.



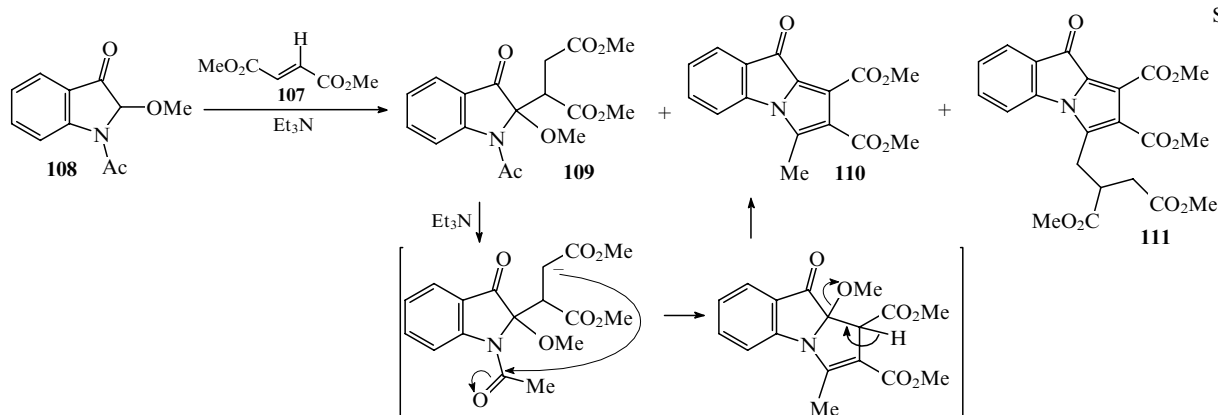
$R = \text{H, Alk.}$

The tandem 'conjugate addition – aldol condensation' sequence has been used in the synthesis of the β -lactam fragment of thienamycin (**103**).⁴⁷ The highly stereoselective conjugate addition of lithium (*R*)-(α -methylbenzyl)allylamide (**104**) to an unsaturated ester, viz., to (*E*)-*tert*-butylpenta-2,4-dienoate (**105**), followed by aldol condensation with acetaldehyde (**106**) led to assembly of all three stereocentres of azetidinone **103** with the required absolute stereochemistry.



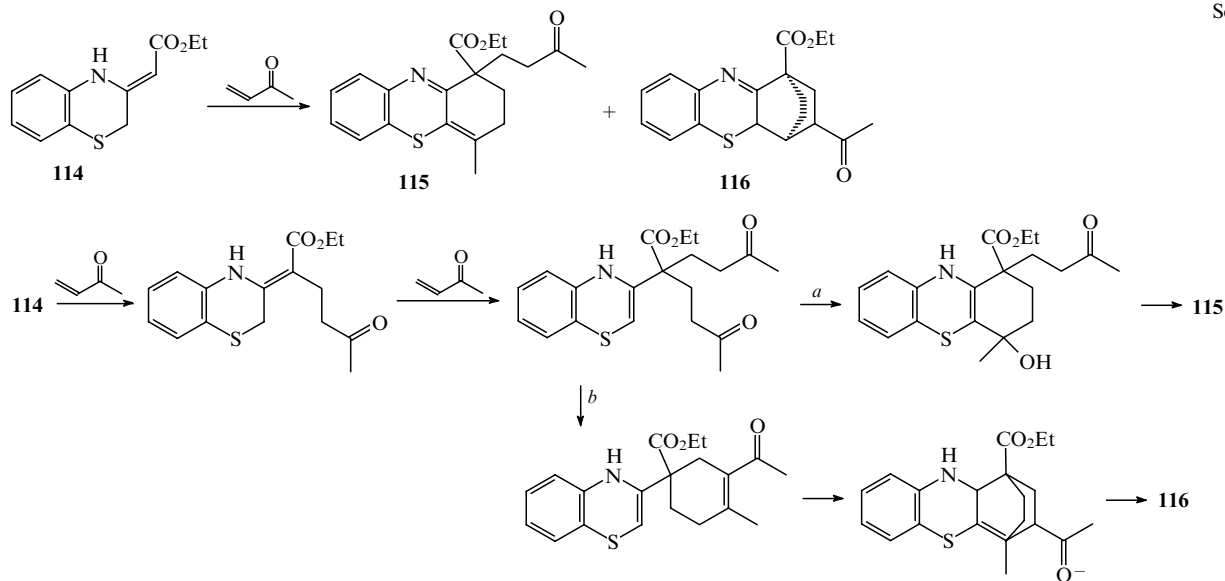
The tandem 'Michael addition – aldol reaction' and 'Michael addition – aldol reaction – Michael reaction' sequences have been described.⁴⁸ Dimethyl fumarate **107** reacted with heterocyclic ketone **108** in the presence of Et_3N to give the expected Michael adduct **109** (the yield was 38%) along with pyrrolo[1,2-*a*]indoles **110** (16%) and **111** (3%) (Scheme 4). Heating of the individual compound **109** with Et_3N afforded the product **110** the formation of which is attributable to spontaneous intramolecular cyclisation of the diester **109** followed by elimination of MeOH . The Michael addition of the pyrrole **110** to the dimethyl fumarate **107** afforded the tetraester **111**.

The 'Michael reaction – intramolecular aldol cyclisation' sequence was used for the synthesis of cycloalkenols **112** from oxo aldehydes **113** under the action of piperidine.⁴⁹ The resulting

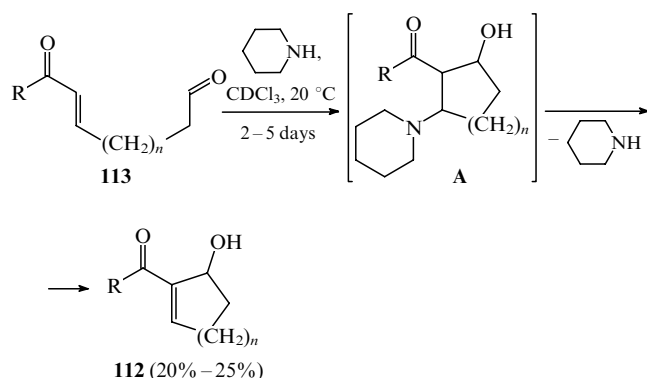


Scheme 4

Scheme 5



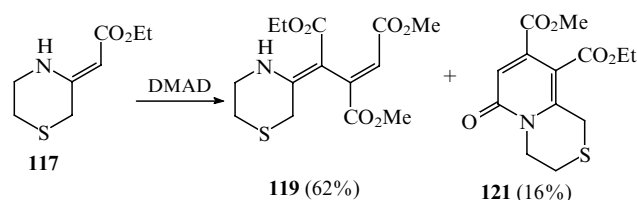
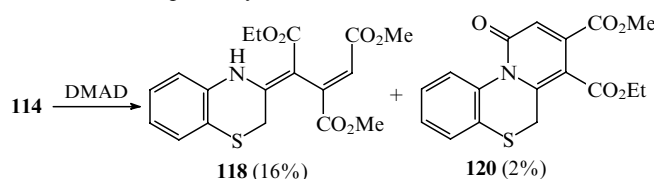
cyclic intermediate **A** (for $R = \text{Ph}$, this intermediate is stable for several days) eliminated piperidine (slowly for $R = \text{Ph}$) to give the enol **112**.



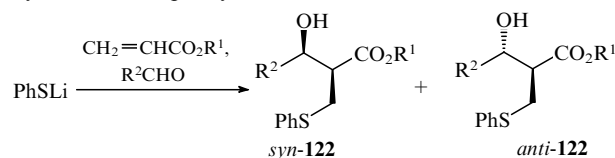
$R = \text{Alk, Ph}; n = 1, 2$.

The reaction of enamine **114** with methyl vinyl ketone at room temperature afforded only the product **115** in 95% yield (Scheme 5).⁵⁰ Refluxing of the reactants gave rise to the tetracycle **116** (the yield was 72%) along with the compound **115** (10%). Apparently, this is attributable to the initial addition of one molecule of methyl vinyl ketone at the α -carbon atom of the enamine followed by isomerisation of the double bond of the adduct and addition of the second molecule of methyl vinyl ketone. The process is completed with intramolecular aldol condensation (path *a*) giving rise to the tricycle **115**. Upon heating, aldol condensation (path *b*) occurs faster than the reaction following the path *a* and product **116** is formed.

The reactions of heterocyclic enamines **114** and **117** with dimethyl acetylenedicarboxylate (DMAD) afforded a mixture of the corresponding Michael addition (**118** and **119**) and cyclisation products (**120** and **121**). The individual compounds **118** and **119** were quantitatively converted upon heating into the cyclic ketones **120** and **121**, respectively.

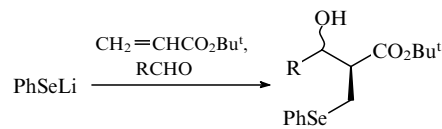


The adduct **122** was obtained in good yield and high *syn*-selectivity by the reaction of a mixture of lithium thiophenoxide, an α,β -unsaturated ester and an aldehyde.⁵¹ The reaction began with the nucleophilic attack of the thiolate at the β -carbon atom of the acceptor giving rise to intermediate enolate which entered into the aldol reaction with the aldehyde to form the polyfunctionalised adduct **122** as a mixture of the *syn*- and *anti*-isomers. An analogous mixture of isomers was obtained in the reaction with the use of lithium selenolate generated *in situ* under the action of methyl lithium on diphenyl selenide.



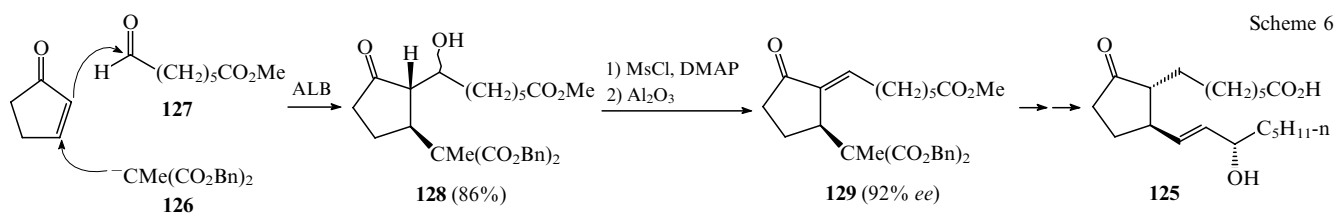
$\text{R}^1, \text{R}^2 = \text{H, Alk.}$

syn : *anti* = 9 : 1

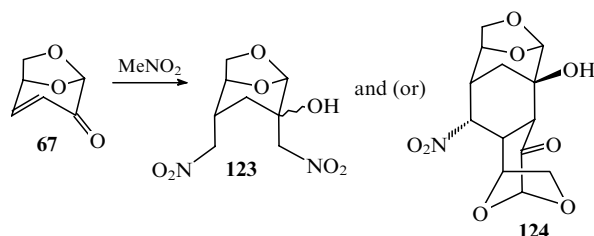


$\text{R} = \text{H, Alk.}$

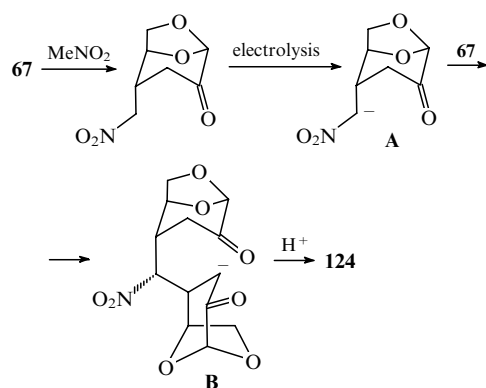
Previously, it had been demonstrated that the reaction of levoglucosenone (**67**) with an excess of nitromethane afforded the addition product **123** (the yield was 89%). The reaction in the presence of an excess of levoglucosenone gave rise to the adduct **124** (95%).³¹ The reaction with the use of an equimolar mixture of the reagents gave both products **123** and **124** in 18% and 61% yields, respectively.³² The electrochemical method proved to be more selective.³⁴ Electrolysis of an equimolar mixture of nitromethane and levoglucosenone afforded exclusively the ketone **124** (the yield was 92%).



MsCl is mesyl chloride; DMAP is dimethylaminopyridine.



The assumed mechanism of formation of the adduct **124** involves the Michael addition of the anion **A**, which is generated by the addition of the nitromethane molecule to the ketone **67**, to the second levoglucosenone molecules followed by intramolecular aldol condensation of the intermediate diketone **B**.



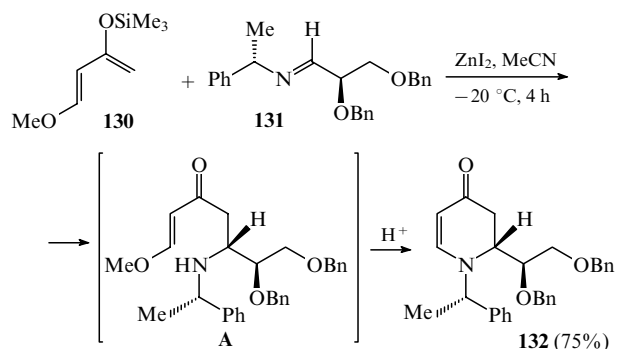
The 'Michael reaction–aldol reaction' sequence was used as the key stage in the synthesis of the prostaglandin 11-deoxy-PGF_{1α} (**125**).⁵² The reaction of cyclopent-2-en-1-one with dibenzyl methylmalonate (**126**) and the aldehyde **127** in the presence of aluminium lithium bis[(*S*)-1,1'-bi-2-naphthoxide] (ALB) as a catalyst produced the expected three-component coupling product **128** as a mixture of two diastereomers in a ratio varying from 6:1 to 17:1. The use of this catalyst not only initiates tandem conversions, but also provides high stereoselectivity of addition. Mesylation of the adduct **128** followed by elimination of MsOH afforded optically pure compound **129**, which can be converted into the target product **125** (Scheme 6).

V. Tandem Mannich and Michael reactions

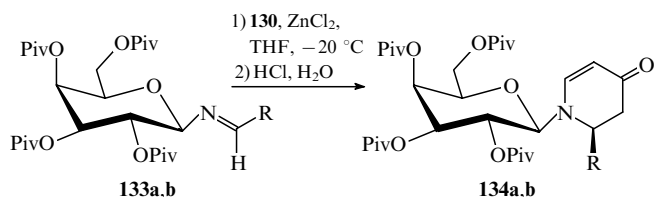
It is known that Mannich bases are very convenient intermediates in a number of syntheses. These bases can readily be converted into vinyl ketones and used in the Michael reaction as electrophiles. Due to their proneness to polymerisation, acceptors are generated from Mannich bases *in situ*. Since decomposition of Mannich bases produces secondary amines, which can catalyse the Michael reaction, an additional amount of base need not be added.

The Mannich and Michael reactions of imines with the Danishefsky diene proceed in tandem.⁵³ Electron-excessive 1-methoxy-3-trimethylsilyloxybutadiene (**130**) reacted with the imine **131** in the presence of a Lewis acid to give the addition product **A**. Acid treatment of the latter led to rapid intramolecular

Michael addition and elimination of MeOH to form cyclic enaminone **132**.

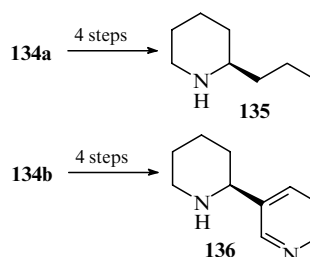


The tandem Mannich and Michael reactions were used for the enantioselective synthesis of chiral piperidine derivatives.⁵⁴ Aldimines derived from tetra-*O*-pivaloyl-β-D-galactopyranosylamine (**133a,b**) and the diene **130** gave 2-substituted dehydropiperidine derivatives **134a,b**, respectively. The latter were transformed into alkaloids coniine (**135**) and anabasine (**136**).

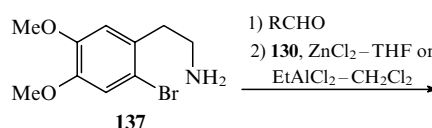


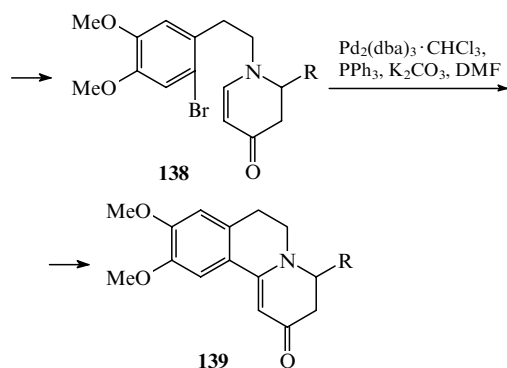
Piv = C(O)CMe₃.

Compounds 133 and 134	R	Yield of 134 (%)
a	Pr ⁿ	96
b	3-Pyridyl	90



An efficient and short procedure was developed for the synthesis of tetra- and hexahydrobenzoquinolizinones, which are precursors of psychoactive alkaloids of the berberine series.⁵⁵ The Mannich and Michael reactions of 2-bromohomoveratrylamine (**137**) and silyoxydiene **130** gave rise to *N*-substituted enaminone **138**, which underwent Heck cyclisation to form the heterocycle **139**.

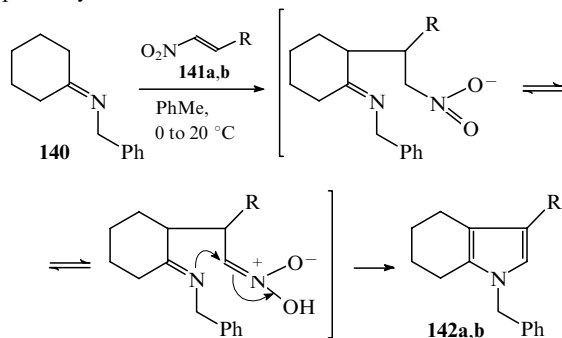




R = H, Alk or Ar; dba is dibenzylideneacetone.

VI. Tandem Michael reaction and heterocyclisation

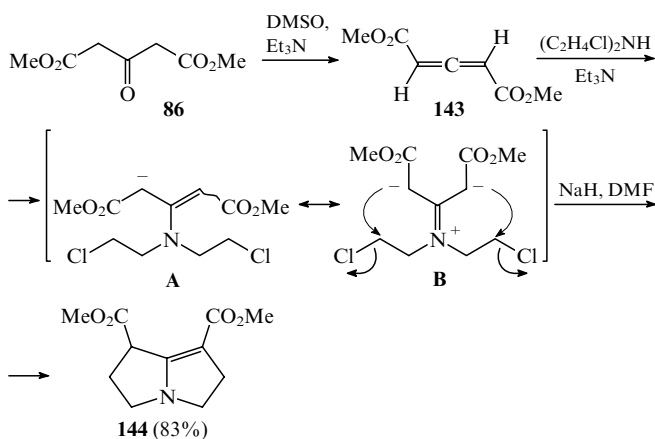
The Michael addition of cyclohexanimines (which react as enamines) to β -substituted nitroalkenes is accompanied by cyclisation and elimination of the nitro group to form substituted tetrahydroindoles.⁵⁶ The imine **140** reacted with *trans*- β -nitro alkenes **141a,b** to give the expected tetrahydroindoles **142a,b**, respectively.



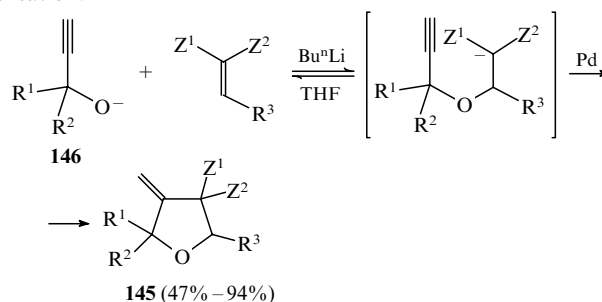
Compounds **141** and **142** R Yield of **142** (%)

a	Ph	70
b	Et	76

Allene-1,3-dicarboxylate (**143**) acts as an extremely reactive acceptor in the Michael reaction. This compound reacts with secondary amines to give the ion **A** as a result of conjugate addition. The ion **A** can also exist as the dianion **B**. The latter contains a good leaving group and undergoes smooth cyclisation. The final product, *viz.*, azabicyclic **144**, represents a skeleton of pyrrolizidine alkaloids.⁵⁷

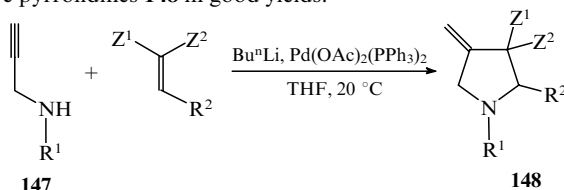


The procedure for the synthesis of various different functionalised 3-methylidenetetrahydrofurans **145**⁵⁸ is based on the conjugate addition of anions of propargylic alcohols **146** to alkylidene- or arylmethylidenemalonate initiated by catalytic amounts of a base and subsequent *in situ* Pd-catalysed *exo-dig* cyclisation.



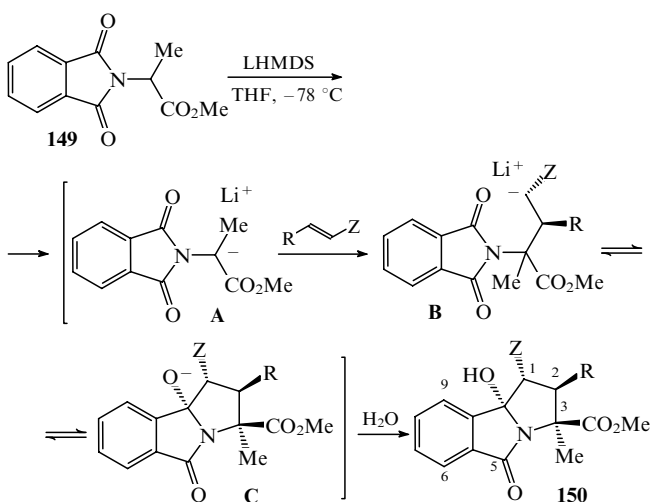
R¹, R² = H, Alk, Ar; R³ = Alk, Ar; Z¹, Z² = CO₂Et, CN.

This approach was used in the synthesis of 3-methylidenepyrrolidines **148**.⁵⁹ *N*-Substituted propargylamine **147** is used as the nucleophilic substrate, which reacts with different acceptors to give pyrrolidines **148** in good yields.



R¹, R² = Alk, Ar; Z¹, Z² = CO₂Et, CN.

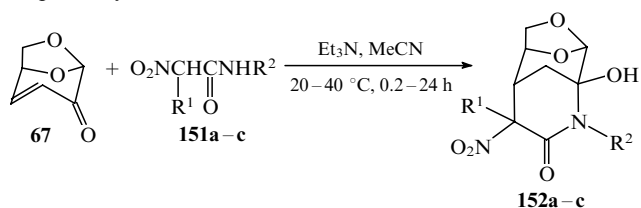
The tandem 'Michael addition – intramolecular condensation' sequence was used in the synthesis of functionalised pyrroloisindoles.⁶⁰ Treatment of methyl ester of *N*-phthaloylalanine (**149**) with lithium hexamethyldisilazide afforded carbanion **A**, which reacted with α,β -unsaturated compounds to give intermediates **B** and **C** and then pyrrolo[2,1-*a*]isindol-5-ones (**150**) according to a standard scheme.



R = H, CO₂Et; Z = CO₂Et, CN.

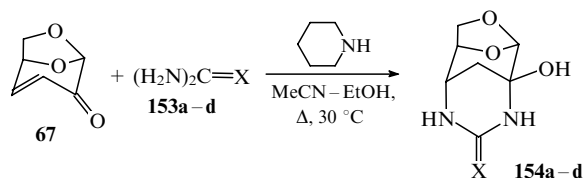
The reactions of levoglucosenone (**67**) with binucleophiles proceed with the participation of the C=C and C=O bonds and can be used for the synthesis of fused heterocyclic systems containing the carbohydrate fragment. Thus the addition of nitroacetamide (**151a**) to levoglucosenone was accompanied by cyclisation to yield exclusively the stereoisomer **152a**.³⁴ The reactions of *N*-hexylnitroacetamide (**151b**) and α -nitropropion-

amide (**151c**) with levoglucosenone produced compounds **152b,c**, respectively.⁶¹



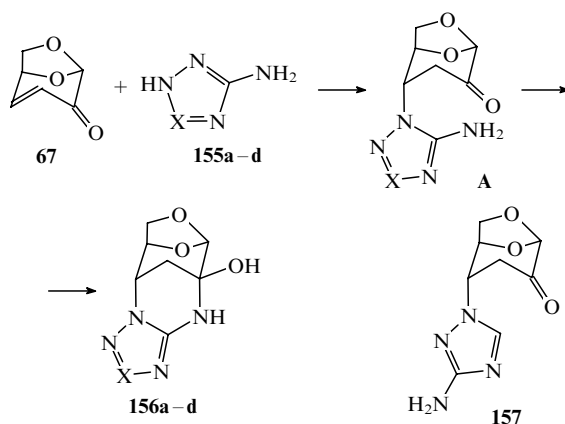
Compounds 151 and 152	R ¹	R ²	Yield of 152 (%)
a	H	H	62
b	H	(CH ₂) ₅ Me	49
c	Me	H	69

The reactions of levoglucosenone with urea (**153a**), thiourea (**153b**), *N*-cyanoguanidine (**153c**) and *N*-nitroguanidine (**153d**) in the presence of bases were accompanied by pyrimidine-ring closure to form compounds **154a-d**, respectively.⁶² In spite of drastic reaction conditions, water was not eliminated from the molecule **154**, as in the above-considered reaction, which is in agreement with the Bredt rule.



Compounds 153 and 154	X	Yield of 154 (%)
a	O	58
b	S	53
c	NCN	31
d	NNO ₂	48

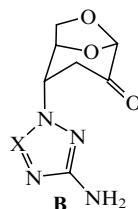
The reactions of levoglucosenone with α -aminoazoles **155a-d** gave rise to azolo[1,5-*a*]pyrimidine systems **156a-d**, respectively.⁶³ In the reaction with the triazole **155b**, the Michael adduct **157** was also formed.



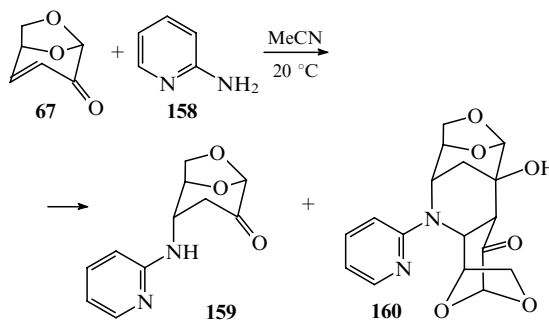
Compounds 155 and 156	X	Yield of 156 (%)
a	N	75
b	CH	39
c	CNO ₂	76
d	CCF ₃	62

Apparently, deprotonation of the NH group of the heterocycle under the action of the base results in the anion, which attacks the double bond of levoglucosenone. If the C=C bond is subjected to the attack of the nitrogen atom adjacent to the amino group, the reaction is not terminated at the stage of formation of

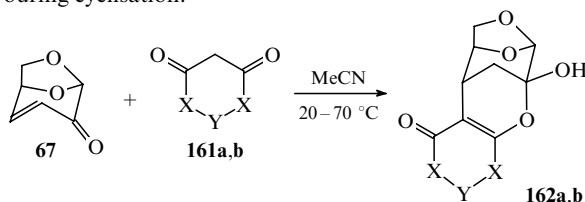
the intermediate **A** and the latter undergoes cyclisation to give compound **156**. On the contrary, if the C=C bond is subjected to attack by the nitrogen atom remote from the amino group (the intermediate **B**), cyclisation does not take place because it should lead to the closure of the seven-membered ring, which is much less probable than the closure of the six-membered ring.



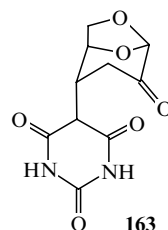
The reaction of levoglucosenone with 2-aminopyridine (**158**) was examined.⁶³ If the reagents were taken in an equimolar ratio, the reaction gave rise to a mixture of the addition product **159** and polycyclic compound **160**. The reaction with a twofold molar excess of levoglucosenone afforded virtually exclusively the product **160**. The compound **160** is structurally very similar to the 2:1 adduct of levoglucosenone with nitromethane, and, consequently, the probable mechanism of its formation involves the addition of two levoglucosenone molecules at the nucleophilic centre followed by intramolecular aldol condensation.



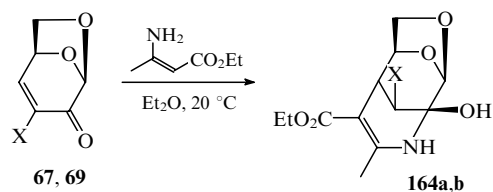
The reaction of levoglucosenone with dimedone (**161a**) yielded only the product **162a**. The reaction of levoglucosenone with barbituric acid (**161b**) produced the tetraketone **163** along with the heterocyclisation product **162b**. The formation of pyrans of the type **162** in the reactions of dimedone or barbituric acid with compound **67** may result from the enhanced reactivity of the carbonyl group of levoglucosenone as well as from steric factors favouring cyclisation.



X = CH₂, Y = CMe₂ (**a**); X = NH, Y = CO (**b**).



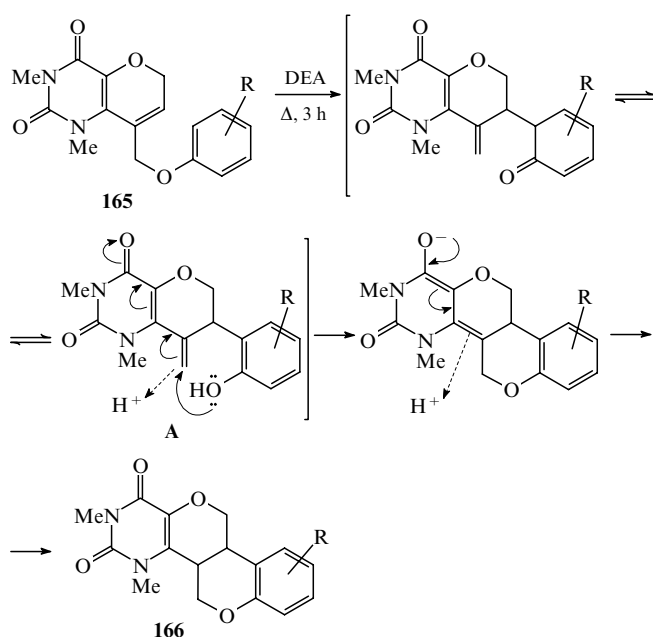
Six-membered hemiaminals **164a,b** smoothly formed in the reactions of the enamine derived from ethyl acetoacetate with levoglucosenone (**67**)⁶³ and 3-iodolevoglucosenone (**69**), respectively.³⁶



X = H (**67, 164a**), I (**69, 164b**).

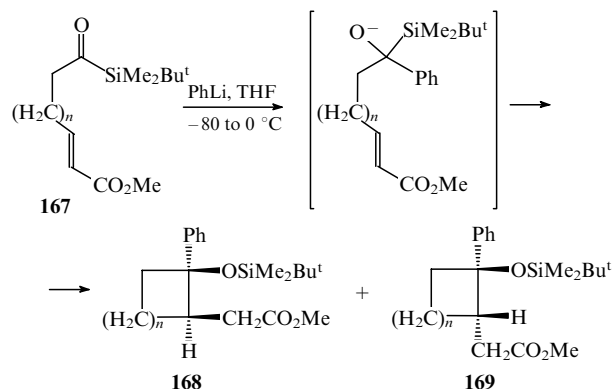
VII. Tandem ‘anionotropic rearrangement – Michael reaction’ sequence

Heating of diketones **165** with *N,N*-diethylaniline (DEA) to 200 °C afforded pyranopyrans **166**.⁶⁴ Apparently, the compound **165** undergoes a sigmatropic rearrangement upon heating to give intermediate **A**, which can undergo intramolecular Michael cyclisation giving rise to the final product **166** due to the suitable arrangement of the phenolic OH group.



R = H, Alk, Cl, NO₂.

The tandem ‘Brook rearrangement – intramolecular Michael reaction’ sequence is suitable for the construction of functionalised carbocycles.⁶⁵ Acylsilanes containing the double bond at a suitable position (separated by 2, 3 or 4 carbon atoms) serve as substrates for cyclisation. The addition of phenyllithium to a solution of the acylsilane **167** brings about the Brook rearrangement and the intramolecular Michael reaction, which proceed smoothly to form diastereomeric cycloalkanes **168** and **169** in a total yield of 70%–82%.

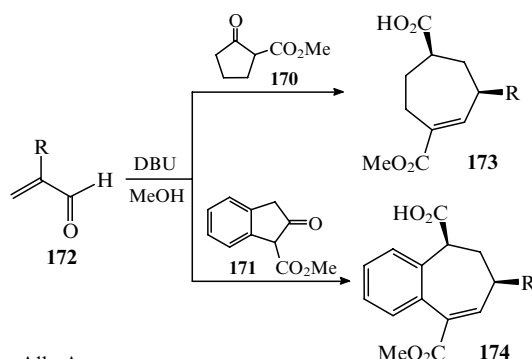


n = 1–3.

VIII. Tandem Michael and Dieckmann reactions

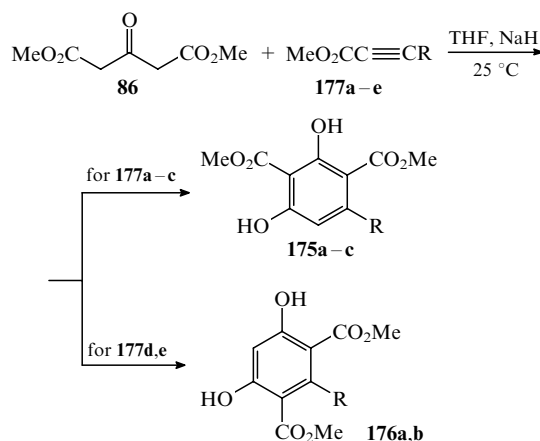
The cascade processes involving more than three different reactions remain poorly studied. Of these processes, the ‘Michael reaction – aldol condensation – retro-Dieckmann reaction’ sequences, which are also called MARD cascades, have received the most study.

Previously, it has been demonstrated⁶⁶ that the reactions of α-oxocyclopentanecarboxylates with acroleins under mild conditions were accompanied by two-carbon-atom ring expansion. The five-step domino reactions of simple cyclic β-oxo esters **170** and **171** with 2-substituted acroleins **172** were used for the synthesis of valuable highly substituted cycloheptenones **173** and **174**, respectively, containing two stereocentres, the double bond and two chemically different carbonyl groups.⁶⁷ The transformation cascade involves the Michael addition, intramolecular aldol condensation and retro-Dieckmann reaction followed by dehydration and chemoselective saponification of one ester group. The configurations of the asymmetric centres are determined by the stereo-differentiating stage of the aldol cyclisation.



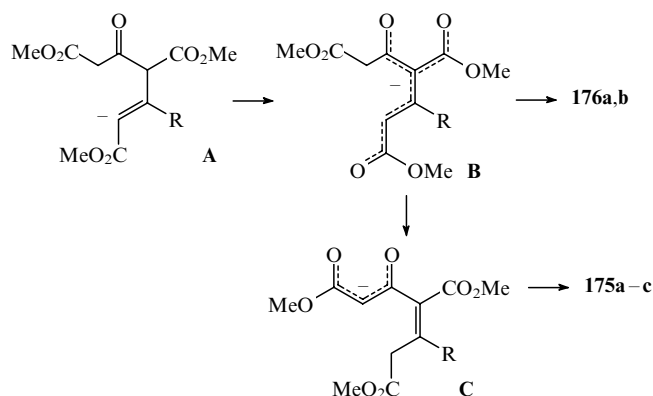
R = Alk, Ar.

The synthesis of non-symmetrical and symmetrical resorcinols **175** and **176** from aliphatic compounds by the tandem ‘Michael reaction – Dieckmann cyclisation’ sequence was investigated.⁶⁸ The reactions of dimethyl 3-oxoglutarate (**86**) with alkyl alkynoates **177a–c** at 25 °C produced non-symmetrical resorcinols **175a–c**, respectively. The reactions with the use of methyl alkynoates **177d,e** at low temperatures afforded symmetrical resorcinols **176a,b**, respectively. Apparently, conjugate addition of the enolate **86** to methyl alkynoates **177a–e** affords vinyl

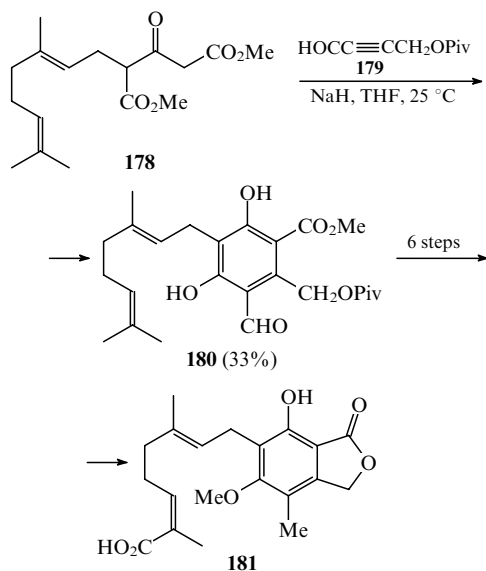


Compound 177	R	Product	Yield (%)
a	Me	175a	59
b	Ph	175b	84
c	CH ₂ OBz	175c	67
d	H	176a	18
e	CO ₂ Me	176b	34

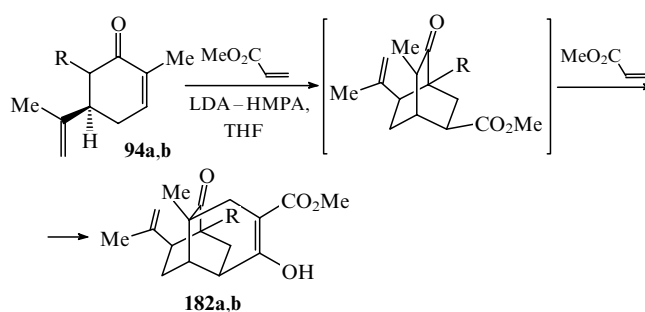
carbanion **A**. The latter is rapidly protonated with the most acidic methylene proton to give carbanion **B**, which is a precursor of symmetrical products **176a,b**. Contrary to the expected stability, the anion **B** underwent isomerisation (at 25 °C) to form enolate **C**, which is a precursor of the non-symmetrical products **175a–c**. It is believed that the delocalised anion **B** is more rapidly generated from the vinyl carbanion **A** and is stable only at low temperatures (up to 0 °C). On the contrary, this anion undergoes isomerisation to give the more stable enolate at room temperature. Consequently, the enolate **A** undergoes cyclisation to form symmetrical resorcinols **176a,b** when low temperature is required for prevention of polymerisation.



The tandem ‘Michael addition–intramolecular Dieckmann cyclisation’ sequence was used as the key stage in the total synthesis of mycophenolic acid exhibiting fungicidal, antibacterial, antiviral and immunosuppressive properties.⁶⁹ The reaction of dimethyl 2-geranyl-3-oxoglutarate (**178**) with 4-pivaloyloxybut-2-ynal (**179**) gave rise to the totally substituted resorcinol **180** with the required arrangement of all substituents. The resulting adduct was converted into the target mycophenolic acid (**181**) in six steps.



The use of readily accessible optically pure α,β -unsaturated ketones, such as carvone (**94a**) or methylcarvone (**94b**), in the tandem sequence of three Michael reactions and Dieckmann cyclisation allows the preparation of optically pure tricyclo[5.3.1.0^{3,8}]undecanes **182a,b**,⁷⁰ which are structural cores of seychellane.

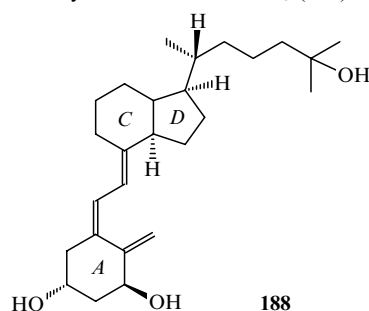


Compounds 94 and 182	R	Yield of 182 (%)
a	H	40
b	Me	44

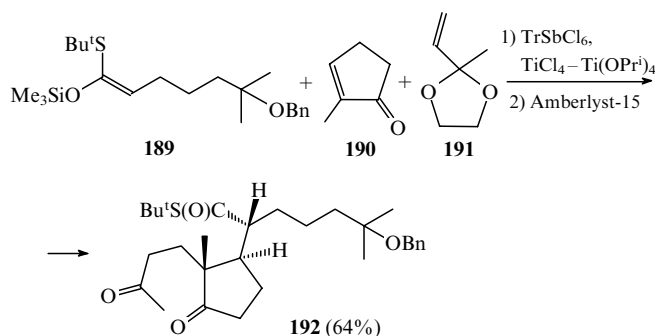
IX. Tandem Mukaiyama and Michael reactions

The tandem ‘Mukaiyama reaction–Michael reaction–aldol cyclisation’ sequence was used as the key stage in the synthesis of biologically active compound **183**.⁷¹ Under conditions of the Mukaiyama reaction, enol silyl ether **184** and spiro compound **185** gave enolate **A** whose conjugate addition to the chalcone **186** afforded enolate **B**. Intramolecular aldol condensation of the latter gave rise to compound **187** from which the target product **183** was obtained (Scheme 7).

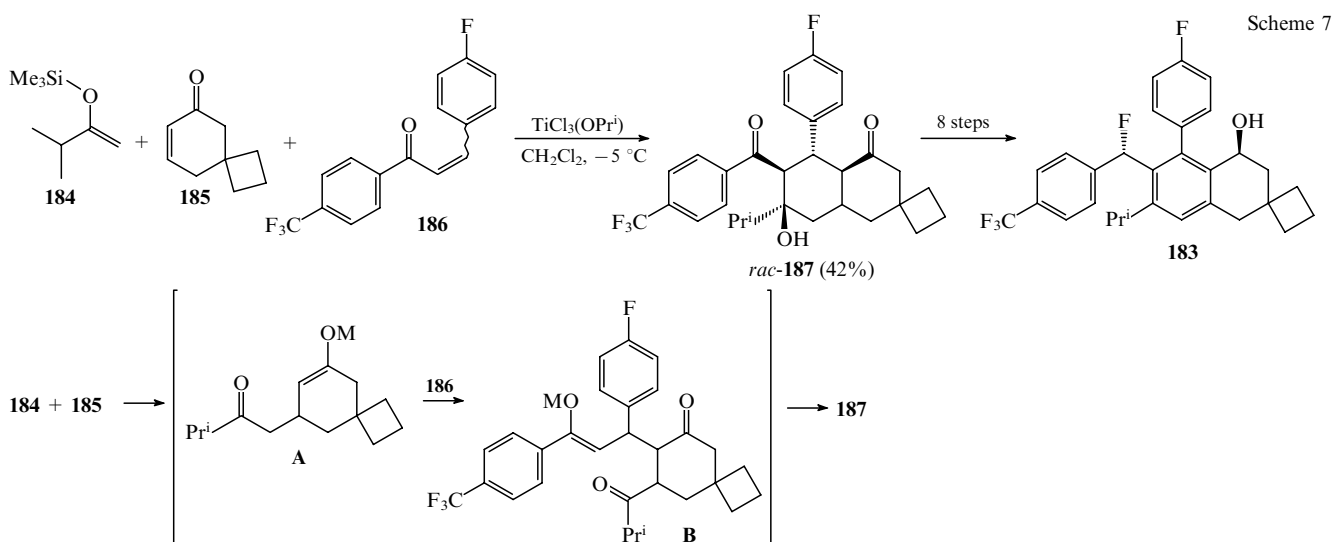
The tandem Michael and Mukaiyama reactions were used in the total synthesis of vitamin D₃ (**188**).⁷²



The reaction of ketene hemithioacetal **189** with 2-methylcyclopent-2-enone (**190**) catalysed by a Lewis acid afforded enol silyl ether. The latter entered into the second conjugate addition reaction with methyl vinyl ketone acetal **191** as a reactive intermediate. The key precursor of blocks of the C/D type (**192**) was prepared in one step starting from three components.

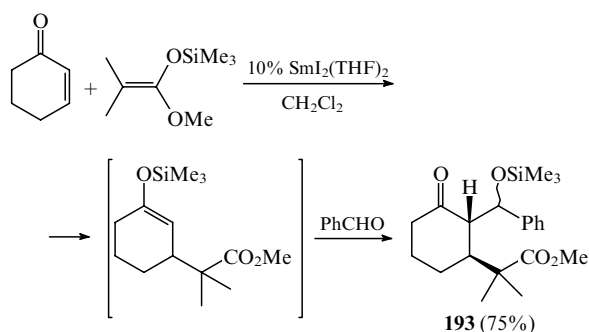


The tandem ‘Mukaiyama–Michael reaction–Mukaiyama reaction–aldol reaction’ sequence was used for the introduction of two chains at the α and β positions of cyclic α,β -unsaturated ketones.⁷³ The low temperature at which this reaction was performed (–60 °C) hindered the formation of by-products of the crotonic type and enabled the achievement of high dia-



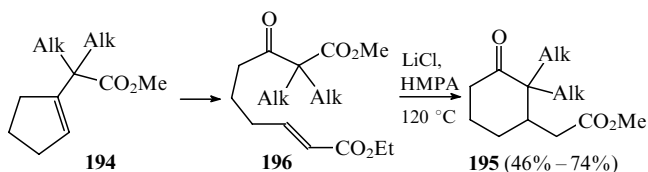
M is a group stabilising enolate.

stereoselectivity (*cis* : *trans* = 98 : 2) and good yields of the adduct **193**. This reaction is the first example of the lanthanide-catalysed tandem formation of C–C intermolecular bonds.



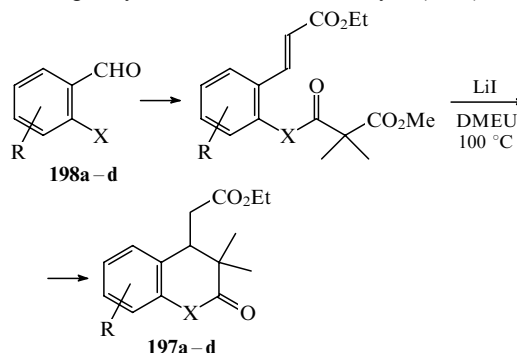
X. Miscellaneous tandem transformations involving Michael reactions

Recently, a large number of new tandem reactions have been developed. Thus a three-step ring expansion was used for the conversion of methyl dialkylcyclopent-1-en-1-ylacetate **194** into methyl cyclohexylacetate **195**.⁷⁴ The process involved ozonolytic cleavage of the double bond in **194**, the Wittig olefination of the product and the tandem sequence of dealkoxycarbonylation of the oxo ester **196** and the Michael addition. Intramolecular cyclisation gave rise to the ester **195**.



An analogous sequence was used for the preparation of lactones and lactams.⁷⁵ Precursors of lactones **197a–c** were synthesised from the corresponding salicylaldehyde derivatives **198a–c** by introducing the acrylic-acid fragment using the Wittig

olefination and esterification of the 2-OH group for the subsequent ring closure. The precursor of the lactam **197d** was synthesised analogously from 2-aminobenzaldehyde (**198d**).

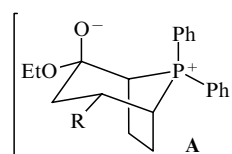


DMEU is 1,3-dimethyl-2-imidazolidinone.

Compounds 197 and 198	R	X	Yield of 197 (%)
a	H	O	62
b	5-OMe	O	50
c	3,4-benzo	O	52
d	H	NH	76

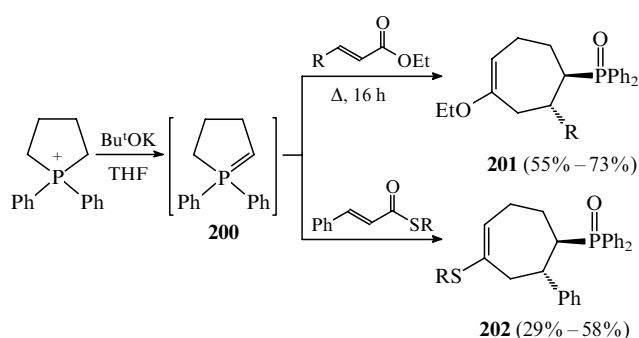
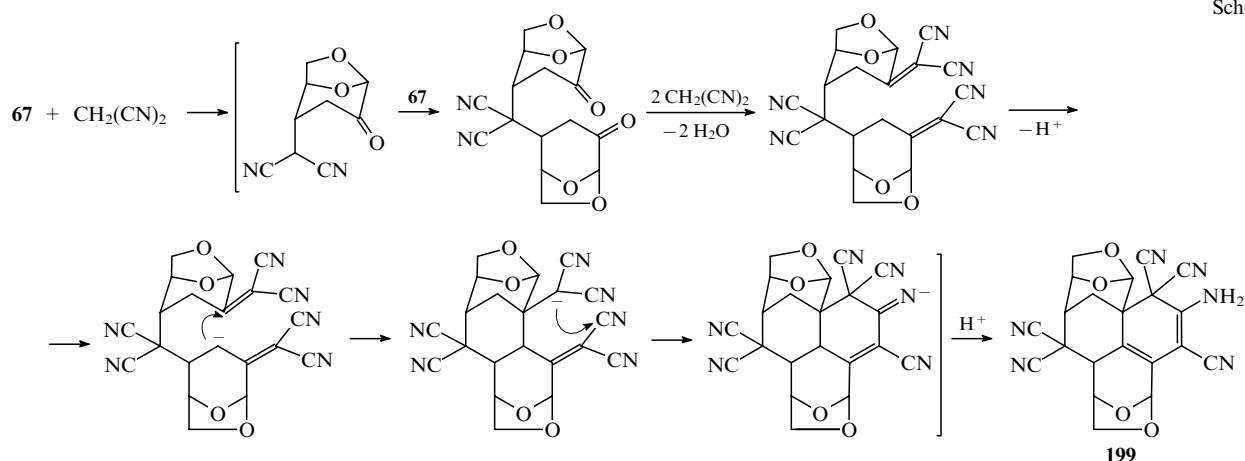
The reaction of levoglucosenone with malononitrile in the presence of piperidine afforded polycyclic compound **199** (Scheme 8).⁷⁶

The tandem Michael and Wittig reactions involving five-membered phosphonium ylides **200** and α,β -unsaturated esters gave rise to seven-membered vinyl ethers **201**.⁷⁷ The process occurred *via* the structurally rigid phosphorus-containing bicyclic intermediate **A**



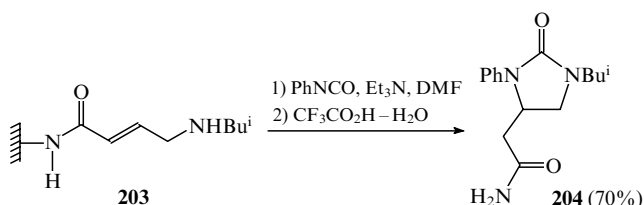
which provided high stereoselectivity of the formation of vinyl ethers. Analogous reactions were observed in the case of α,β -unsaturated thioesters⁷⁸ yielding cycloheptene derivatives **202**.

Scheme 8

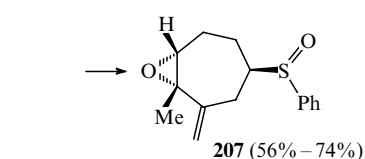
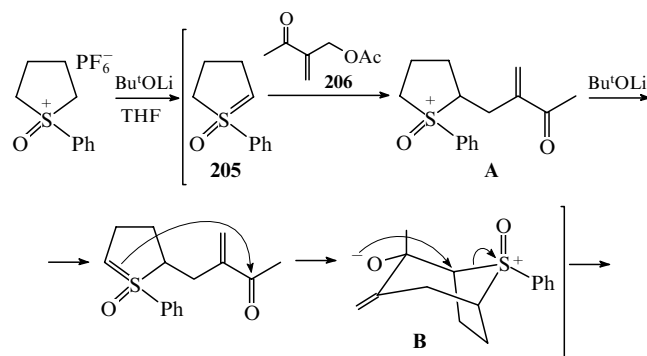


R = Alk, Ar.

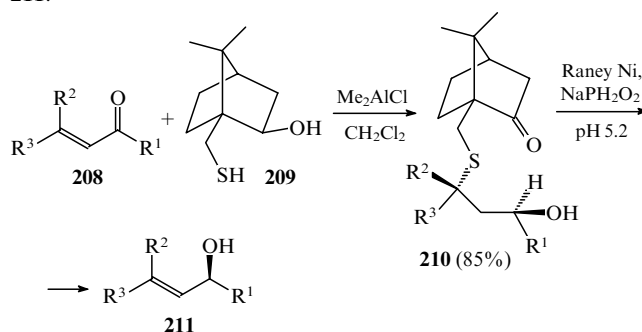
A new procedure was developed for the solid-phase synthesis of imidazolidin-2-ones with the use of the tandem ‘aminoacylation–Michael addition’ sequence.⁷⁹ The reaction of the allylic amine **203** bound to an ion-exchange resin with phenyl isocyanate proceeded regioselectively to form imidazolidin-2-one **204**.



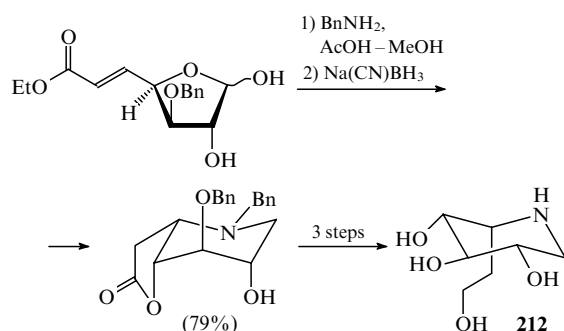
The tandem Michael and Corey–Chaykovsky reactions of five-membered oxosulfonium ylides **205** with β -acetoxy- α -methylidene ketones **206** produced cycloheptene oxide derivatives **207**.⁸⁰ Initially, the Michael addition of the ylide **205** to the enone **206** occurred. Then the acetoxy group was eliminated to form the cation **A** followed by generation of the ylide and the intramolecular Corey–Chaykovsky reaction, which proceeded *via* the stable intermediate **B**. The latter was converted into epoxide **207**.



The tandem ‘Michael addition–Meerwein–Ponndorf–Verley reduction’ sequence was used for the asymmetric reduction of α,β -unsaturated ketones giving rise to secondary alcohols.⁸¹ The reaction of the enone **208** with (–)-10-mercaptoisoborneol (**209**) in the presence of Me_2AlCl afforded the expected product **210**. In this tandem process, the chiral mercaptoalcohol reacted with enone to give an adduct, which was converted into the alcohol **210** as a result of intramolecular proton transfer. Reductive desulfurisation of the latter produced the optically active alcohol **211**.

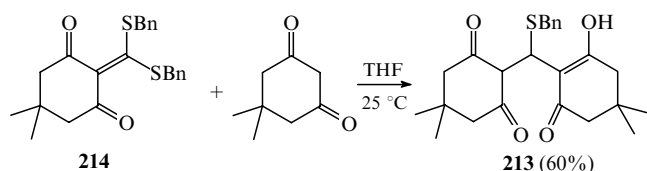
R¹, R², R³ = H, Alk, Ar.

The three-step ‘reductive amination–intramolecular Michael reaction–lactonisation’ sequence was used for the construction of the ring skeleton of homoaza-sugars in the synthesis of higher homologues of 1-deoxy-L-ido-nojirimycin (**212**) exhibiting a broad spectrum of biological activities.⁸² Apparently, reductive amination of the anomeric centre was succeeded by intramolecu-

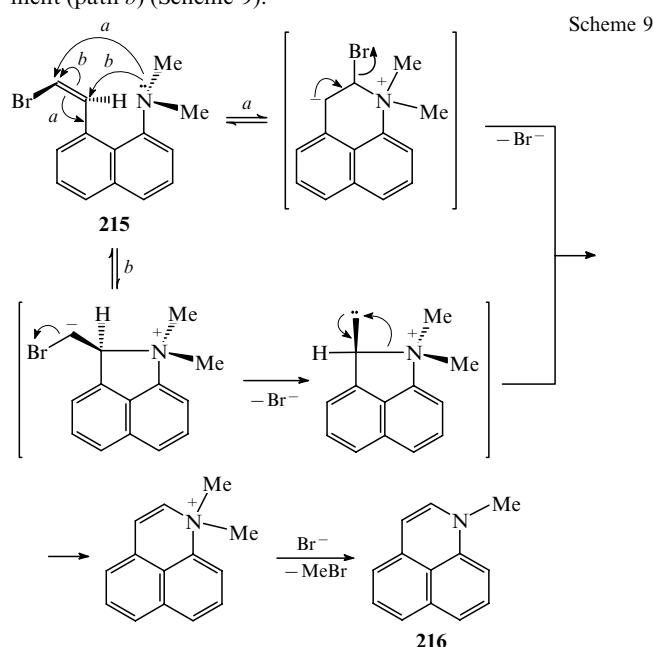


lar ring closure at the activated double bond and lactonisation. Reduction of the ester group and deprotection gave rise to the target product **112**.

The tandem Michael addition and elimination were used as the key stages in the total synthesis of the S-containing yellow pigment of Australian sponges, *viz.*, benzylthiocrellidone (**213**),⁸³ which was prepared by the reaction of ketene dithioacetal **214** with dimedone.

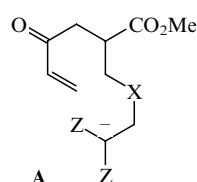


The transformation of *cis*-1-bromo-2-(1-naphthyl)ethylene containing the dimethylamino group at the *peri* position (**215**) into *N*-methylbenzo[*de*]quinoline **216** was studied.⁸⁴ The tandem addition–elimination reactions can follow two alternative pathways, *viz.*, 6-*endo-trig* addition–elimination (path *a*) or tandem 5-*exo-trig* Michael addition followed by the carbene rearrangement (path *b*) (Scheme 9).



A new approach to the synthesis of 9–15-membered cyclic compound was devised.⁸⁵ Very dilute solutions of substrates **217–219** were treated with cesium fluoride, which induced a sequence of ring opening and ring closure reactions to yield cyclopentadecanone, cyclotetradecanone and cyclononanone derivatives (**220**, **221** and **222**), respectively (Scheme 10).

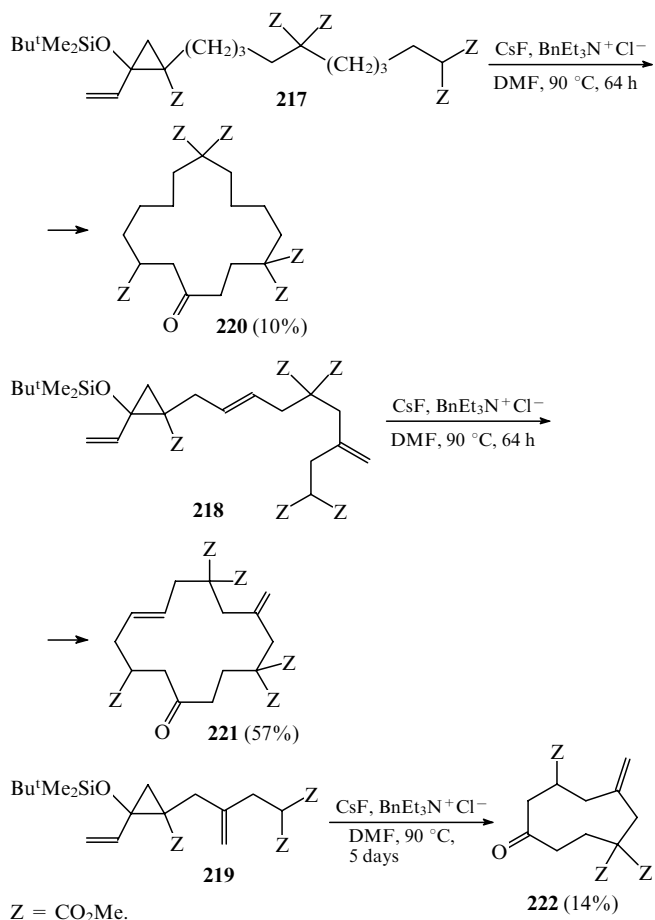
The efficiency of the intramolecular Michael addition, which is the crucial step and consists in the transformation of the carbanion **A** into the final product, depends essentially on the ‘bridging’ X group.



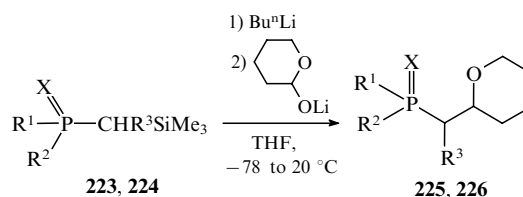
X = (CH₂)₂, CH = CH.

The tandem Peterson and Michael reactions have been described.⁸⁶ The reactions of α -silyl- α -formyl carbanions with carbonyl compounds containing a nucleophilic group gave rise to

Scheme 10



cyclic compounds with a functionalised side chain. Tandem reactions of α -trimethylsilylalkylphosphine oxide (**223**) or α -trimethylsilylalkylphosphine sulfide (**224**) with *n*-butyllithium and then with lithium tetrahydropyran-2-olate gave rise to products **225** and **226**, respectively, in high yields.



X = O (**223**, **225**), S (**224**, **226**); R¹, R², R³ = H, Ar.

* * *

To summarise, tandem transformations, which represent an advantageous combination of the thermodynamic and kinetic parameters of a single process, play an important role in procedures for the preparation of complex organic compounds. There is no doubt that the development of one-pot tandem reactions based on compounds containing various functional groups resulting in substantial complication of the starting structures is an important problem of modern organic synthesis.

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Methods of synthesis of conjugated ω -amino ketones

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Abstract. The published data on the synthesis of β -enamino ketones, δ -amino dienones and conjugated ω -amino polyenones of diverse structures are generalised. The bibliography includes 129 references.

I. Introduction

Conjugated ω -amino ketones represent an ample class of organic compounds which attract the attention of a broad circle of organic chemists, biochemists, physicochemists, *etc.* Owing to their high reactivities, these compounds find application in the synthesis of various biologically active heterocyclic systems, natural compounds, dyes and photosensitive materials.

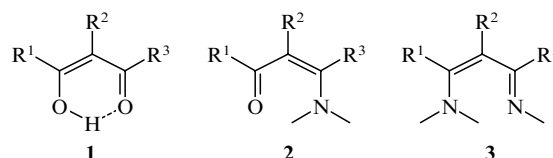
The presence in ω -amino ketones of an electron-donating and an electron-withdrawing group separated by conjugated double bonds imparts to them specific properties and makes them perfect models for the study of fundamental problems, such as the nature of chemical bonds, electron transfer along the conjugation chain, chromaticity, sensitivity to the action of different kinds of energy, tautomerism, *cis-trans*-isomerism, *etc.*

The methods employed in the synthesis of β -aminovinyl ketones (AVK) have been generalised in reviews^{1,2} and the monograph by Freimanis.³ Several novel versions of conventional reactions which make it possible to increase the yields of the target products and to simplify the synthetic procedures have been proposed recently. The approaches to regio- and stereospecific synthesis of enamino ketones containing additional functional groups are being developed intensively. The most practicable methods for the synthesis of AVK and those based on unusual chemical conversions are considered in this review. Special attention is given to conjugated ω -amino polyenones prepared with the help of procedures developed in recent years. These compounds include α,α' -bis(ω -aminopolyenyl)alkanones, which contain two polymethine chains linked through a carbonyl group and manifest unusual spectral and luminescent properties.

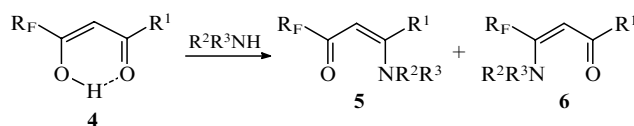
II. Methods of synthesis of β -aminovinyl ketones, δ -amino dienones and α,α' -bis(3-aminopropenylidene)alkanones

1. Reactions of β -diketones with amines

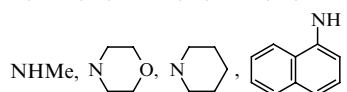
Condensation of readily accessible β -diketones with ammonia and amines is a traditional approach to the synthesis of β -aminovinyl ketones.^{1–8} The starting diketone reacts in both diketo- and keto-enol forms. This reaction is usually carried out by boiling β -diketone–amine mixtures in solvents (*e.g.*, benzene, toluene) which allow removal of the water formed.^{4–7} In the reaction of non-symmetrical β -diketones **1** ($R^1 \neq R^3$), one or both regioisomeric AVK **2**, β -aminovinylimine **3** or their mixture can be formed due to the non-equivalence of the electrophilic centres C(1) and C(2).^{1,3,6–8}



The difference in the reactivities of the electrophilic centres C(1) and C(3) is especially pronounced in the case of non-symmetrical polyfluorinated β -diketones **4** due to the difference in the inductive effects of the substituents R_F and R^1 (Refs 6–8). Polyfluorinated β -diketones **4** react with ammonia and amines at only one of the electrophilic centres to give fluorine-containing AVK **5**.^{6–8}



$R_F = CF_3, H(CF_2)_2, H(CF_2)_4$; $R^1 = Me, Bu^a, Bu^t, Ph, C_6H_4Cl, C_6H_4Br, C_6H_4NO_2, C_3H_4Me, C_6H_4OMe$; $R^2R^3N = NH_2, NHPh$,



It is of note that the condensation of arylfluoroalkyl diketones **4** with NH_3 , NH_2Me and NH_2Ph affords a mixture of regioisomeric AVK **5** and **6**; the proportion of the isomer **6** with a geminal amino group and the fluoroalkyl residue depends on the length of the fluoroalkyl substituent and the nature of substituents in the amine.^{7,8} This reaction is carried out with azeotropic distillation of the water eliminated. In the case of low-boiling amines, this reaction is difficult to perform, since this requires repeated

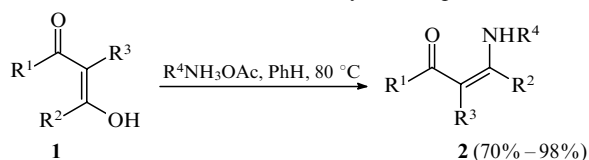
Yu V Smirnova, Zh A Krasnaya N D Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prosp. 47, 119992 Moscow, Russian Federation. Fax (7-095) 135 53 28. Tel. (7-095) 135 89 61. E-mail: yusmir@cacr.ioc.ac.ru (Yu V Smirnova), kra@cacr.ioc.ac.ru (Zh A Krasnaya)

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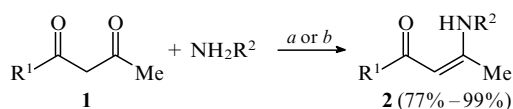
bubbling of the amine into the reaction mixture for the reaction to complete.^{4,6,7,9} This reaction is also accompanied by scission of the β -diketones at the C(1)–C(2) bond and by secondary condensations.^{1,8} Therefore, modifications of the process^{10–14} which exclude the formation of by-products, increase the selectivity and simplify the procedure are of special interest.

Thus, a method for the synthesis of AVK **2** was proposed which includes boiling 1,3-diketones with ammonium acetate or acetates of low-boiling amines in benzene in the presence of AcOH; the water formed is removed by azeotropic distillation.¹⁰



$\text{R}^1 = \text{Me, Ph; R}^2 = \text{Me; R}^3 = \text{H, CH}_2\text{CH}=\text{CH}_2$;
 $\text{R}^2-\text{R}^3 = (\text{CH}_2)_3, \text{CH}_2\text{CH}(\text{Me})\text{CH}_2$; $\text{R}^4 = \text{H, Et}$.

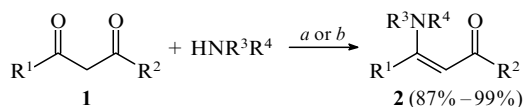
Satisfactory results were obtained in the condensation of methyl diketones with primary amines on inorganic supports.^{11,12} Under heterogenous conditions, the reactions proceed with higher selectivities and under milder conditions than the corresponding homogenous reactions.



$\text{R}^1 = \text{Me, Ph; R}^2 = \text{H, Me, Et, Bu}^t, \text{Pr}^i, \text{Ph, Bn, CH}_2\text{CN}$;
 (a) Al_2O_3 ; (b) montmorillonite K10.

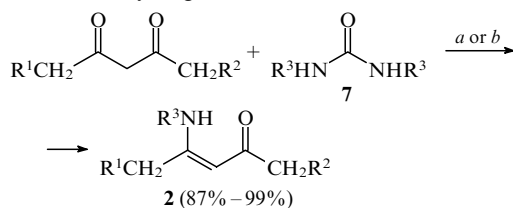
Neutral alumina or montmorillonite K10 can be used as solid supports. The reagents must be completely adsorbed on the support. This procedure is extremely simple as regards its implementation. To isolate enamino ketones **2**, the reaction mixture is diluted with CH_2Cl_2 , the solid phase is filtered off, the solvent is removed *in vacuo* and the residue is subjected to distillation. In reactions with acetyl acetone (**1**, $\text{R}^1 = \text{Me}$), primary amines can be used as aqueous solutions, which is especially important in the case of low-boiling amines.¹²

If heterogenous reactions are carried out in a microwave (MW) oven,^{13,14} the reaction time decreases from 24 h to 1–20 min. Both primary and secondary amines can be introduced into the reaction.¹³



$\text{R}^1 = \text{R}^2 = \text{Ph, R}^3-\text{R}^4 = (\text{CH}_2)_4, (\text{CH}_2)_5$; $\text{R}^1 = \text{Me, R}^2 = \text{Ph, OMe}$;
 $\text{R}^3-\text{R}^4 = (\text{CH}_2)_4$; (a) SiO_2 , MW, 1–20 min; (b) montmorillonite K10, MW, 1–20 min.

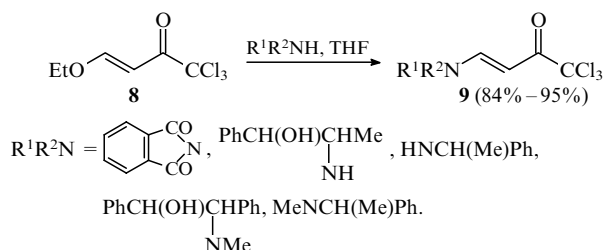
It was shown¹³ that primary amines yield acyclic AVK **2** with *Z*-configuration of the α,β -double bond. The use of symmetrical disubstituted ureas **7**¹⁴ instead of amines also results in AVK **2** having a *Z*-configuration of the double bond and stabilised by an intramolecular hydrogen bond.



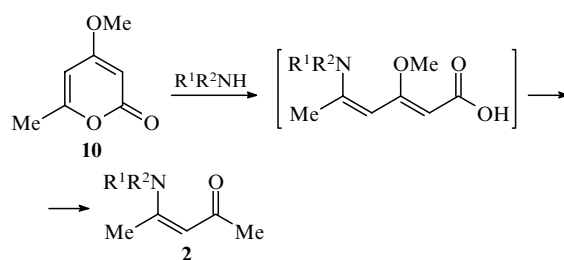
$\text{R}^1 = \text{R}^2 = \text{Me, Ph; R}^3 = \text{H, Me, Et, Ph}$; (a) SiO_2 , MW, 1–20 min;
 (b) montmorillonite K10, MW, 1–20 min.

2. Reactions of unsaturated alkoxy ketones with amines

The alkoxy group in readily accessible β -alkoxyvinyl ketones **8**^{15–18} is exchanged for an amino group upon reactions with ammonia and primary and secondary amines.^{3,18–22} This reaction is widely employed in the synthesis of halogen-containing AVK **9**.^{18–22} As a rule, the reaction of amines with β -alkoxyvinyl ketones proceeds at room temperature or with gentle heating and results in high yields of AVK **9** even in the case of sterically hindered amines.^{15,19–22}



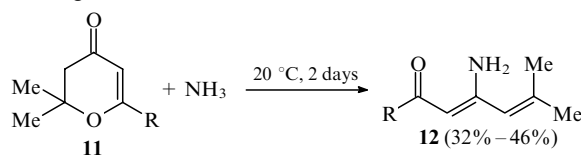
The reactions of alkoxy-substituted *2H*- and *4H*-pyrones with amines also belong to this type of transformations.^{3,23–25} Thus prolonged boiling of 6-methyl-4-methoxy-2-pyrone **10** with amines in the absence of solvents resulted in the formation of AVK **2**.²⁴ The details of these experiments have not been reported.



$\text{R}^1 = \text{H; R}^2 = \text{C}_7\text{H}_{15}$; $\text{R}^1-\text{R}^2 = (\text{CH}_2)_4$.

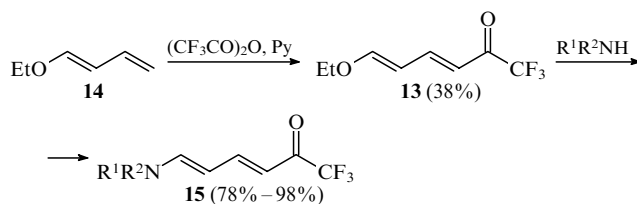
It is believed²⁴ that AVK **2** are formed as a result of an attack by the amine at position 6 of the pyrone ring with subsequent decarboxylation and hydrolysis of the diacetoacetic acid derivative.

Treatment of dihydropyrones **11** with aqueous or methanolic ammonia gives amino dienones **12**.²⁵



$\text{R} = \text{CF}_3, \text{CCl}_3$.

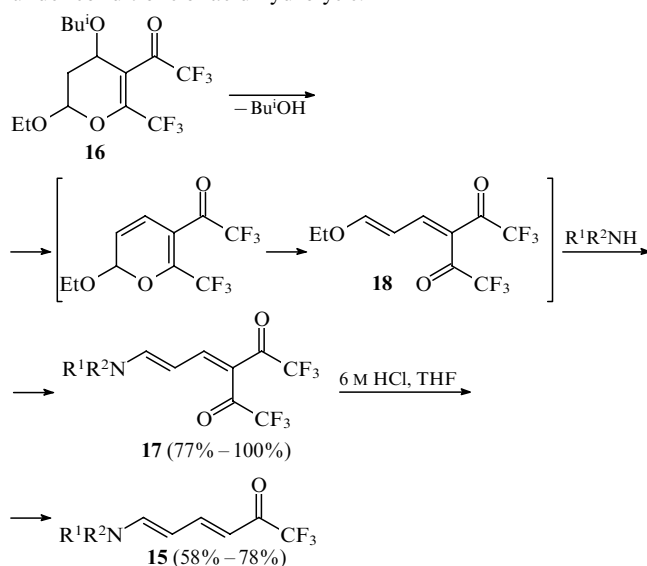
δ -Alkoxy hexadienone **13** obtained by the acylation of 1-ethoxybuta-1,3-diene (**14**) with trifluoroacetic anhydride reacts with amines much like β -alkoxyvinyl ketones.²⁶ The alkoxy group in the dienone **13** is readily exchanged for an amino group to give δ -amino dienones **15**.



$\text{R}^1 = \text{R}^2 = \text{H, Et; R}^1 = \text{Me, R}^2 = \text{Ph}$.

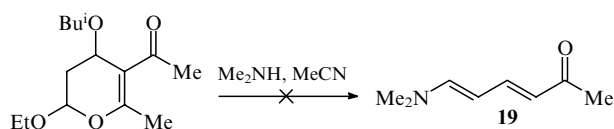
δ -Amino dienones **15** were also prepared²⁷ from 3,4-dihydro-*2H*-pyran derivative **16**. Compound **16** reacts with various aliphatic and aromatic amines to give substituted diketones **17**. Presumably,²⁷ the putative mechanism of this reaction involves

ethoxy-substituted dienedione **18** as an intermediate. Acid hydrolysis of diketones **17** with aliphatic substituents at the nitrogen atom results in δ -amino dienones **15**. Diketones **17** with aromatic substituents at the nitrogen atom do not undergo deacetylation under conditions of acid hydrolysis.



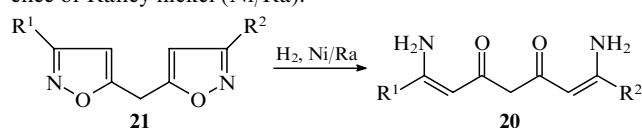
$\text{R}^1 = \text{R}^2 = \text{Me, Et, Bn}$; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Ph}$; $\text{R}^1 - \text{R}^2 = (\text{CH}_2)_4, (\text{CH}_2)_5$.

Non-fluorinated derivatives of 3,4-dihydro-2H-pyran do not react with amines. An attempt to apply this approach to the synthesis of 6-dimethylaminohexa-3,5-dien-2-one (**19**) was unsuccessful.²⁷



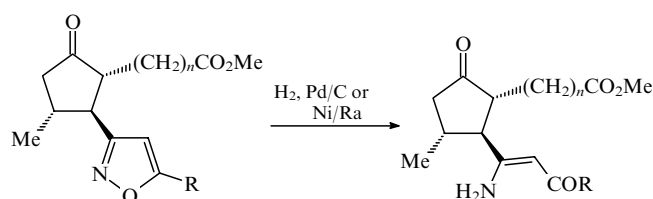
3. Reductive cleavage of isoxazoles

Reductive cleavage of the isoxazole ring under conditions of catalytic hydrogenation is one of the most well-studied and widely employed procedures for the preparation of enamino ketones.^{28–31} Diaminodivinyl diketones **20** were obtained by the reduction of the diisoxazolylmethane derivatives **21** in the presence of Raney nickel (Ni/Ra).



$\text{R}^1 = \text{R}^2 = \text{Me, Ph}$; $\text{R}^1 = \text{Ph}$, $\text{R}^2 = \text{Me}$.

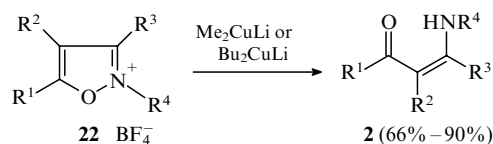
Catalytic hydrogenation of isoxazoles affords enamino ketones selectively, other functional groups of the starting compounds are not affected.³¹



$n = 3, 5$; $\text{R} = \text{C}_5\text{H}_{11}, \text{CH}_2\text{OC}_6\text{H}_4\text{F-2}$.

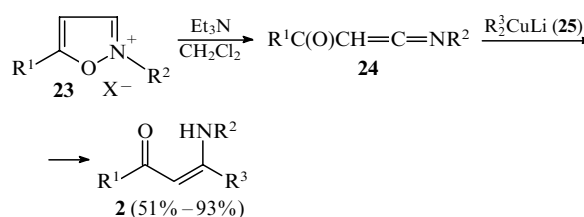
The enamino ketones **2** were obtained in good yields by reductive cleavage of 3,4,5-substituted isoxazolium salts **22** with lithium dialkyl cuprates generated *in situ* from methyl- or butyllithium and copper iodide.³² This reaction proceeds very quickly

and under very mild conditions (-20°C , 15 min) and affords enamino ketones **2** with different (including functional) substituents in the α -position.³²



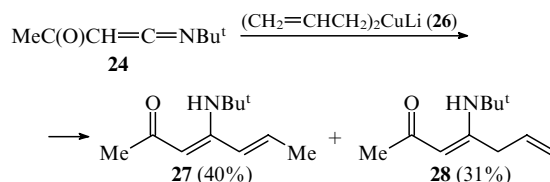
$\text{R}^1 = \text{R}^3 = \text{R}^4 = \text{Me, Ph}$; $\text{R}^2 = \text{H, Br, Cl, CPh, COMe, CO}_2\text{Et, CN, NO}_2$.

More readily accessible 5-substituted isoxazolium salts **23** do not react with lithium cuprates. In this case, preliminary treatment with triethylamine resulting in oxo ketene imines **24** is required. The reactions of the latter with organocuprates **25** afford AVK **2**, simultaneously a substituent is introduced into the β -position of the AVK formed.³³



$\text{X} = \text{ClO}_4, \text{BF}_4^-$; $\text{R}^1 = \text{Me, Ph}$; $\text{R}^2 = \text{Bu}^t, \text{Et}$; $\text{R}^3 = \text{Me, Bu}^n, \text{Bu}^t, \text{Ph}$.

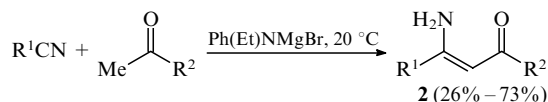
The reaction of oxo ketene imine **24** ($\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Bu}^t$) with lithium diallyl cuprate (**26**) leads to the isomerisation of the allyl group into the propenyl group to yield a mixture of enamino ketones **27** and **28** containing conjugated and isolated double bonds.



4. Condensation of acid nitriles with methyl ketones

Until recently, information concerning the synthesis of AVK by condensation of nitriles with ketones was scarce.^{3, 34} A method for the synthesis of enamino ketones containing a primary amino group from nitriles and methyl ketones has been developed in the last few years where (phenyl)ethylaminomagnesium bromide is used as a condensing reagent. This procedure affords enamino ketones of various structures, which are difficult to prepare by other methods.^{35, 36}

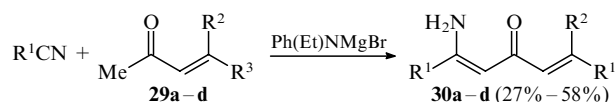
The yields of enamino ketones depend on the nature of substituents in the starting compounds. The best results were obtained in the reaction of trichloroacetonitrile with aryl(hetaryl) methyl ketones and *tert*-alkyl methyl ketones with acid nitriles containing electron-withdrawing aromatic substituents.³⁶



R^1	R^2	Yield (%)	R^1	R^2	Yield (%)
Ph	Bu^t	48	PhOCH_2	Bu^t	48
4-MeOC ₆ H ₄	Bu^t	26	CCl_3	Bu^t	58
4-BrC ₆ H ₄	Bu^t	80	Pr ⁱ	Ph	34
			Ph		73
	Bu^t	60			71
Bn	Bu^t	54			

The presence of a double bond³⁷ or a functional group^{38–46} in the molecule of a methyl ketone does not prevent the reaction with nitriles, the cyano group of which is activated by a polyhalogenoalkyl substituent, which makes it possible to synthesise enamino ketones containing several functional groups.

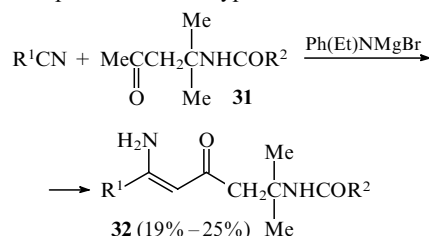
Thus the reaction of trichloro- and trifluoroacetonitriles with α,β -unsaturated ketones **29a–d** results in β -aminodiviny ketones **30a–d**.³⁷



$\text{R}^1 = \text{CCl}_3, \text{CF}_3$; $\text{R}^2 = \text{R}^3 = \text{Me}$ (**a**); $\text{R}^2 = \text{H}$; $\text{R}^3 = \text{Ph}$ (**b**),

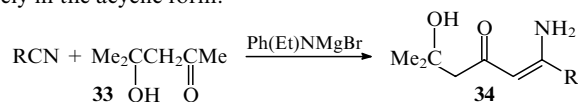
4-MeOC₆H₄ (**c**),  (**d**).

The condensation of β -acylaminoalkyl methyl ketones **31** with halogenoacetonitriles gives AVK **32**.³⁸ This is the first example of the involvement of β -acylaminoalkyl methyl ketones as a methyl-ene component in aldol-type reactions.



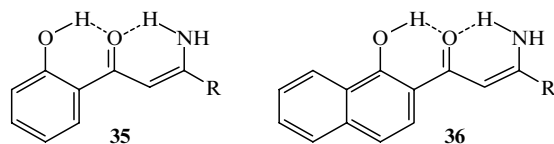
$\text{R}^1 = \text{CCl}_3, \text{CF}_3$; $\text{R}^2 = \text{Me}, \text{Ph}$.

The reaction of trichloro- and trifluoroacetonitrile with the so-called diacetone alcohol **33** proceeds as nucleophilic addition to the nitrile group and yields β -aminovinyl β' -hydroxyalkyl ketones **34**; the latter are stable compounds, which occur exclusively in the acyclic form.³⁹



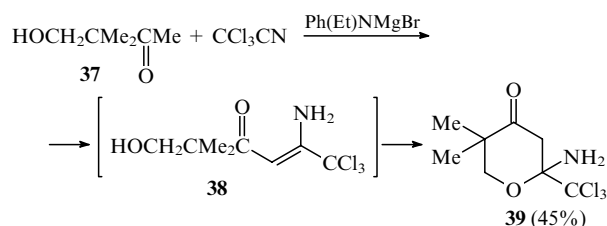
$\text{R} = \text{CCl}_3, \text{CF}_3$.

The condensation of trichloro- or trifluoroacetonitrile with 2-hydroxyacetophenone³⁹ and 2-acetyl-1-naphthol⁴⁰ gives the corresponding hydroxy enamino ketones **35** and **36**, which occur as *Z*-isomers with a coplanar *s-cis*-configuration stabilised by intramolecular hydrogen bonds.



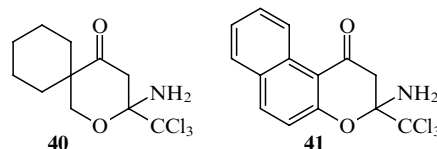
$\text{R} = \text{CCl}_3, \text{CF}_3$.

On going to sterically hindered β -hydroxyalkyl methyl ketones, the structures of the reaction products depend on the nature of the halogen in the halogenoacetonitrile.^{41, 42} Thus the reaction of trichloroacetonitrile with 4-hydroxy-3,3-dimethylbutan-2-one (**37**) is not stopped in the formation of an open form of

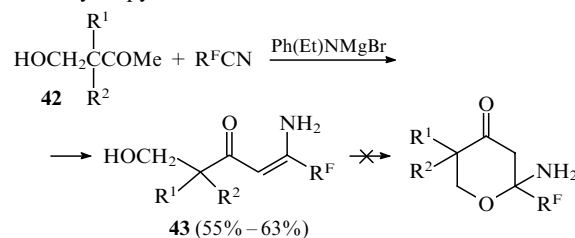


the hydroxy enamino ketone **38**; its spontaneous cyclisation yields tetrahydropyranone **39**.⁴¹

The condensation of trichloroacetonitrile with 1-acetyl-1-hydroxymethylcyclohexane⁴¹ and 1-acetyl-2-naphthol⁴⁰ proceeds similarly to give the cyclic products **40** and **41**. Acyclic forms were absent in both cases.

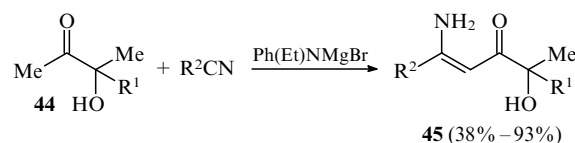


The reactions of polyfluorocarboxylic acid nitriles with sterically hindered β -hydroxyalkyl ketones **42** under the same conditions afford hydroxy enamino ketones **43** as the final products; the latter are stable on storage and do not cyclise spontaneously into tetrahydropyranones.⁴²



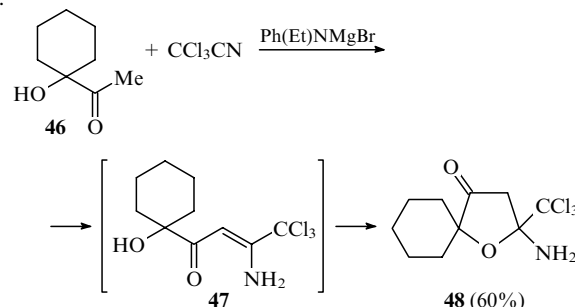
$\text{R}^1 = \text{R}^2 = \text{Me}$, $\text{R}^1-\text{R}^2 = (\text{CH}_2)_5$; $\text{R}^F = \text{CF}_3, (\text{CF}_2)_2\text{H}$.

The reaction of trichloro- and trifluoroacetonitrile with acyclic hydroxyalkyl ketones **44** in the presence of (phenyl)ethylmagnesium bromide results in the corresponding hydroxy enamino ketones **45**.^{43, 44}

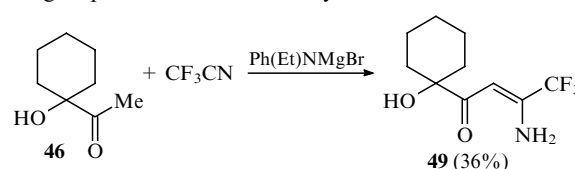


$\text{R}^1 = \text{Me}, \text{Et}, \text{Bu}^t$; $\text{R}^2 = \text{CCl}_3, \text{CF}_3$.

As in the case of sterically hindered β -hydroxyalkyl methyl ketones, the structures of the products formed in the reactions of nitriles with sterically hindered α -hydroxyalkyl methyl ketones depend on the nature of the halogen which activates the cyano group.^{45, 46} Thus the condensation of 1-acetylcyclohexan-1-ol (**46**) with trichloroacetonitrile does not afford α -hydroxy enamino ketone **47** as might be expected, but rather gives its cyclic isomer **48**.⁴⁵



The condensation of α -hydroxy ketone **46** with trifluoroacetonitrile results in α -hydroxy enamino ketone **49** with a geminal amino group and the trifluoromethyl substituent.⁴⁶

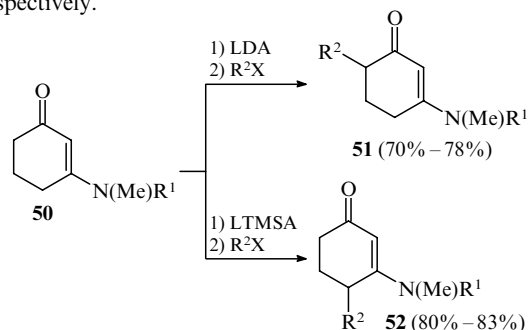


5. Modification of β -aminovinyl ketones based on the use of their lithium salts

Enamino ketones containing other functional groups in addition to the aminoenone group cannot be prepared in the majority of cases using traditional methods.^{2, 3, 19, 21, 31–33} Therefore, procedures based on directed introduction of functional groups into more readily accessible AVK acquire special importance. The use of N,α' - and N,γ -dilithium salts of AVK in reactions with electrophiles is an example of a successful application of synthetic approaches to regio-controlled introduction of functional groups into AVK.

Studies of reactivities of N,α' - and N,γ -dilithium derivatives with respect to various electrophiles have shown that these are convenient starting compounds for the synthesis of heterocyclic compounds and for the introduction of functional groups into the α' - and γ -positions of AVK.^{47–58}

The alkylation of cyclic AVK **50** is the first example of such an approach.⁴⁷ It was shown that depending on conditions of preparation of lithium salts (*viz.*, the reagent ratios, the nature of a base, temperature), the alkylation predominantly occurs either at position 6 or at position 4 to give the AVK derivatives **51** or **52**, respectively.

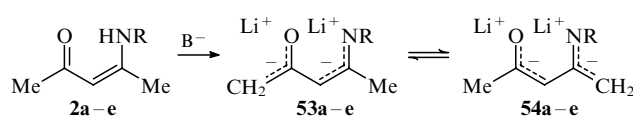


$R^1 = \text{Me}, \text{C}_6\text{H}_{11}$; $R^2 = \text{Bn}, \text{Me}$; $X = \text{I}, \text{Br}$; LDA is lithium N,N -diisopropylamide; LTMSA is lithium bis(trimethylsilyl)amide.

Treatment of the enamino ketone **50** with lithium N,N -diisopropylamide (LDA) in ether or THF at -78°C results in deprotonation of the α' -position to afford a kinetically more favourable dianion (termed an α' -dianion); its alkylation gives rise to the cyclic AVK **51**. Deprotonation of the γ -position which gives a thermodynamically more favourable dianion (termed a γ -dianion) occurs upon treatment of compound **50** with lithium bis(trimethylsilyl)amide (LTMSA). Subsequent alkylation results in a practically exclusive formation of AVK **52**.⁴⁷ However, this approach could not be used for the alkylation of acyclic AVK, since it gave a mixture of alkylation products irrespective of the base used.⁴⁷

The conditions favouring the preparation of α' - or γ -dilithium derivatives from acyclic β -(N -monoalkylamino)vinyl ketones and the factors influencing the regioselectivity of their formation have been studied in detail.^{48, 49}

Treatment of 4-(N -alkylamino)pent-3-enones **2a–e** with an excess of a strong base (2.5 equiv., THF) gives both α' - (**53**) and γ -dilithium derivatives **54** which exist in a dynamic equilibrium (see Ref. 48).[†]

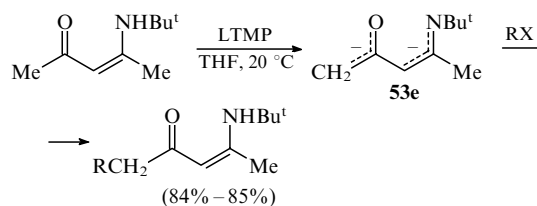


$R = \text{Me}$ (**a**), Pr^i (**b**), cyclo- C_6H_{11} (**c**), PhCHMe (**d**), Bu^t (**e**).

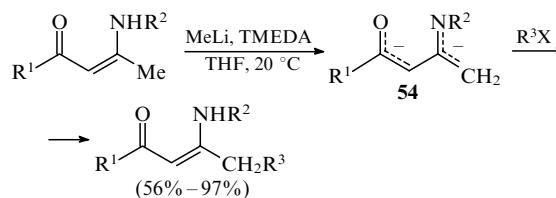
Depending on the strength of the base and the substituent R in the starting compound (AVK **2**), the equilibrium can be practi-

cally completely shifted towards one of the dianions.^{48–51} The α' -dianion **53** which is predominantly formed upon treatment of AVK **2** with lithium 2,2,6,6-tetramethylpiperidide (LTMP) is kinetically more favourable. Thermodynamic calculations demonstrate that under these conditions the conformation of the α' -dianion **53** prevents its isomerisation into a thermodynamically more stable γ -dianion **54**.⁴⁸ It should be noted that the regioselectivity of formation of the α' -dianion **53** depends on the size of the substituent at the nitrogen atom. The predominant formation of the α' -dianion **53** is observed only in the case of bulky substituents, such as Bu^t and Ph .^{49, 51} In the presence of less bulky substituents ($R = \text{Me}, \text{Pr}^i$) the γ -dianion **54** is formed together with the α' -dianion **53**.⁵¹ The predominant formation of a thermodynamically more favourable γ -dianion **54** takes place under the action of a stronger base, *viz.*, methyllithium, in the presence of N,N,N',N' -tetramethylethylenediamine (TMEDA). Under these conditions, the α' -dianion which is formed first adopts a conformation which allows its rapid isomerisation into a more stable γ -dianion **54**.^{48, 51} The size of a substituent at the nitrogen atom does not influence the regioselectivity of formation of the γ -dianion **54**.⁴⁸ The dianions **53** and **54** can also be prepared from enamino ketones with secondary amino groups.^{48–50, 54, 58}

The reactions of the dianions **53** and **54** with electrophiles proceed at low temperatures (-100 to -20°C) and take as a rule from 5 min to 2 h. The alkylation of dianions of the type **53** and **54** afforded the corresponding α' - and γ -alkyl-substituted AVK in good yields. It is noteworthy that this reaction proceeds as C-alkylation and does not affect the primary amino group.^{48, 52}



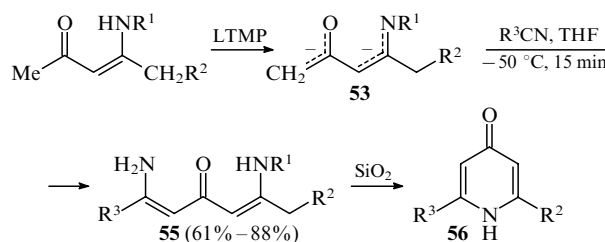
$R = \text{Me}, \text{Bn}$; $X = \text{Br}, \text{I}$.



$R^1 = \text{Me}, \text{Ph}, 4\text{-MeC}_6\text{H}_4, 4\text{-MeOC}_6\text{H}_4$; $R^2 = \text{Me}, \text{Pr}^i, \text{Bu}^t$;
 $R^3 = \text{Me}, \text{Et}, \text{Pr}^i, \text{Bn}, n\text{-C}_{10}\text{H}_{23}, \text{CH}_2\text{CH}=\text{CH}_2, \text{CH}_2\text{C}\equiv\text{CH}$;
 $X = \text{Cl}, \text{Br}, \text{I}$.

In addition to alkyl halides, allyl and propargyl bromides can be used as alkylating agents.⁵²

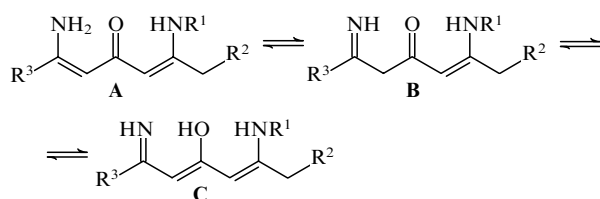
α' -Dianions of the type **53** react smoothly with nitriles under mild conditions to give bis(aminovinyl) ketones **55**. During chromatography on SiO_2 , compounds **55** are partly converted into 4-pyridones **56**. This reaction is quantitative when solutions of enamino ketones are kept over SiO_2 for 2 days.⁵⁰



$R^1 = \text{Pr}^i, \text{Ph}$; $R^2 = \text{Et}, \text{Bn}, \text{H}$; $R^3 = \text{Ph}, \text{Bu}^n, 2\text{-ClC}_6\text{H}_4$.

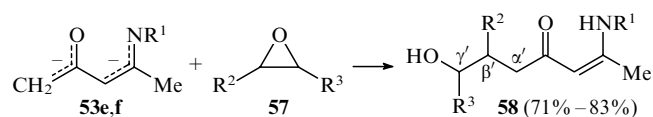
[†] Hereinafter, for convenience sake we shall refer to the dilithium derivatives **53** and **54** as dianions and omit Li cations in the structural formulae.

According to ^1H and ^{13}C NMR and X-ray diffraction data, compounds **55** exist in both solutions and crystalline state as tautomers **A** containing two enamine fragments, but not as oxo- (**B**) or hydroxy imines (**C**).⁵⁰

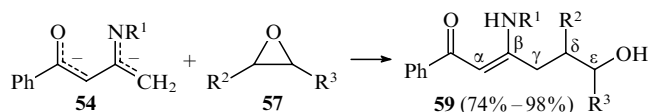


Hydroxy derivatives of enamino ketones were obtained in the reaction of α' - (**53**) or γ -dianions (**54**) with oxiranes,⁴⁹ aldehydes, ketones^{51, 53} and esters.⁵⁴

The reaction of dianions of the type **53** and **54** with oxiranes **57** is accompanied by the opening of the epoxide ring to give the corresponding γ' - or ε -hydroxy derivatives **58** and **59**. This reaction proceeds as bimolecular $\text{S}_{\text{N}}2$ nucleophilic substitution; non-symmetrical epoxides react at the least substituted carbon atom. The opening of the epoxide ring occurs in a stereo- and regioselective manner resulting in only one of the possible isomers.⁴⁹

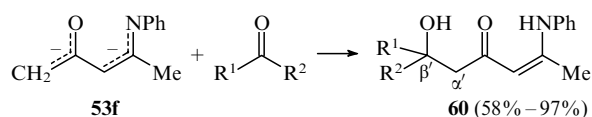


$\text{R}^1 = \text{Bu}^t$ (**53e**), Ph (**53f**); $\text{R}^2 = \text{H}$; $\text{R}^3 = \text{H}, \text{Me}, \text{Et}, \text{Bu}, \text{Ph}$;
 $\text{R}^2-\text{R}^3 = (\text{CH}_2)_4$.



$\text{R}^1 = \text{Me}, \text{Bu}$; $\text{R}^2 = \text{H}, \text{Ph}, \text{Me}_3\text{Si}$; $\text{R}^3 = \text{H}, \text{Me}, \text{Et}, \text{CH}_2\text{Cl}$;
 $\text{R}^2-\text{R}^3 = (\text{CH}_2)_4$.

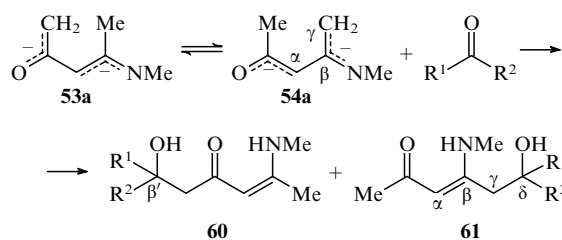
The condensation of the α' -dianion **53f** with aldehydes and ketones was used to obtain β -aminovinyl β' -hydroxy alkyl ketones **60**.⁵¹ Like aminovinyl β' -hydroxyalkyl ketones **34**, these are stable in the acyclic form.



$\text{R}^1 = \text{H}, \text{Me}, \text{Ph}$; $\text{R}^2 = \text{Me}, \text{Pr}, \text{Bu}^t, n\text{-C}_6\text{H}_{13}, \text{Ph}, (\text{CH}_2)_2\text{Ph}$.

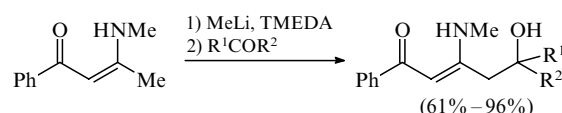
Compounds **60** are produced in high yields even if sterically hindered aldehydes and ketones (trimethylacetaldehyde or benzophenone) and enolisable ketones (*e.g.*, acetophenone) are introduced into the reaction.

In contrast to the α' -dianion **53f**, the condensation of the γ -dianion **54a** with aldehydes and ketones is non-regiospecific and results in the formation of both δ - (**60**) and β' -hydroxyenamino ketones (**61**).⁵¹



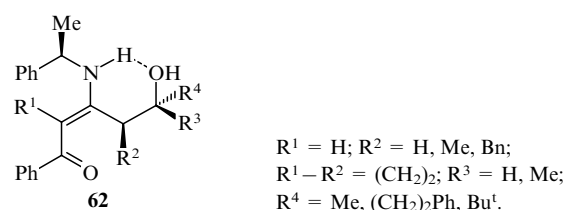
$\text{R}^1 = \text{H}, \text{Me}, \text{Ph}$; $\text{R}^2 = \text{Me}, \text{Pr}^n, \text{Bu}^t, n\text{-C}_6\text{H}_{13}, \text{Ph}, (\text{CH}_2)_2\text{Ph}$,
 $\text{CH} = \text{CHPh}$.

Presumably,^{48, 51} the attack of bulky electrophiles, such as carbonyl compounds, at the sterically hindered γ -position of the γ -dianion **54a** which exists in the *syn*-conformation proceeds with great difficulty. However, owing to the presence in the reaction mixture of a small amount of a more reactive α' -dianion **53a** the latter reacts with carbonyl compounds much faster to give a β' -hydroxy derivative, which is accumulated in the mixture due to rapid isomerisation of the anion **54a**. This suggestion is corroborated by the fact that the yield of the undesirable β' -hydroxy ketone **60** increases in the case of sterically more hindered ketones, *e.g.*, benzophenone.⁵¹ Its formation could be completely excluded using an enamino ketone with a phenyl substituent as a starting compound.



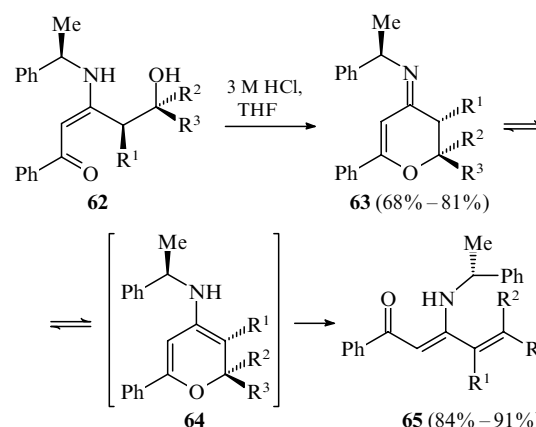
$\text{R}^1 = \text{H}, \text{Me}, \text{Ph}$; $\text{R}^2 = \text{Me}, \text{Et}, \text{Ph}, \text{cyclo-C}_6\text{H}_{11}$.

Direct aldol condensation of γ -dianions of the type **54** with aldehydes and ketones gave chiral *anti*- β -amino- δ -hydroxyalk-1-enyl ketones **62**.⁵³ The stereoselectivity of this reaction depends critically on steric factors, being increased in the case of sterically more hindered starting enamino ketones and carbonyl compounds.⁵³



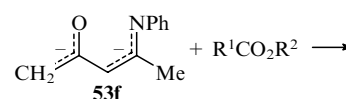
$\text{R}^1 = \text{H}$; $\text{R}^2 = \text{H}, \text{Me}, \text{Bn}$;
 $\text{R}^1-\text{R}^2 = (\text{CH}_2)_2$; $\text{R}^3 = \text{H}, \text{Me}$;
 $\text{R}^4 = \text{Me}, (\text{CH}_2)_2\text{Ph}, \text{Bu}^t$.

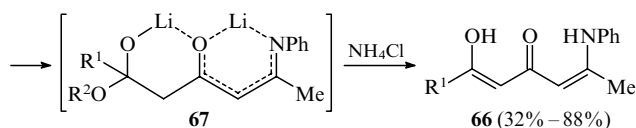
Under conditions of acid hydrolysis, enamino ketones **62** undergo cyclisation into 4-imino-2,3-dihydropyrans **63**. Compounds **63** are stable in acid media, apparently due to the formation of a more stable protonated form **64**. However, in neutral media iminopyrans **63** are unstable and isomerise into enamino ketones **65**.⁵³



$\text{R}^1 = \text{H}, \text{Bn}, \text{Me}$; $\text{R}^2 = \text{Me}, \text{Bu}^t, \text{Ph}$; $\text{R}^3 = \text{H}, \text{Me}$.

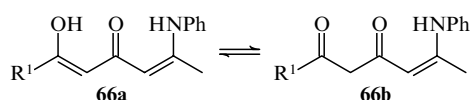
The reaction of the dilithium derivative **53f** with esters results in enamino enols **66**.⁵⁴



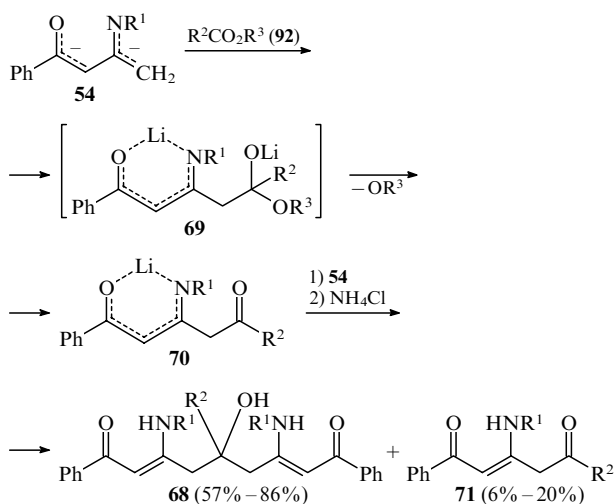


$\text{R}^1 = \text{Ph}, 4\text{-ClC}_6\text{H}_4, \text{EtCHBr}; \text{R}^2 = \text{Me}, \text{Et}, \text{C}(\text{Me})=\text{CH}_2.$

It was proposed⁵⁴ that the adduct **67** stabilised by bridging bonds, is the intermediate in this reaction. The yields of compounds **66** are very high in the case of aromatic acid esters, but decrease dramatically if aliphatic acid esters are used. Moreover, the reaction of dilithium derivatives with aliphatic acid esters is accompanied by the formation of ester self-condensation products; their proportion increases with time. It is suggested⁵⁴ that a transmetallation reaction between the dilithium derivative **53f** and the ester favours self-condensation of esters. According to ^1H NMR spectroscopic data, compounds **66** exist in solutions as two tautomers, *viz.*, ketoenols **66a** and diketones **66b**, the equilibrium being markedly shifted towards the enol form **66a**.⁵⁴

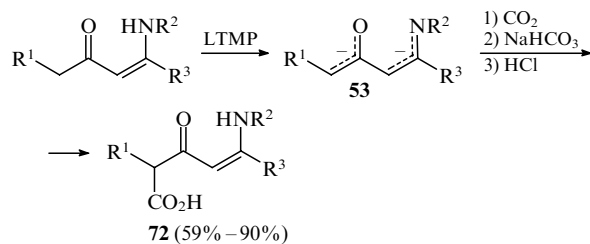


It should be noted that the reaction of dilithium derivatives of the type **54** with esters yields unsaturated amino alcohols **68** as the main product; these are formed as a result of condensation of two molecules of the enamino ketone with one molecule of the ester. Obviously, the intermediate **69** which is formed first is far less stable than the adduct **67** and is decomposed with elimination of the alcoholate anion to give the monolithium derivative **70**. The carbonyl group of the latter is not coordinated with the lithium ion and behaves as the free carbonyl group. Its reaction with the second molecule of the γ -dilithium derivative **54** affords the polyfunctional compounds **68**.⁵⁴ The expected products of this reaction, *viz.*, enamino diketones **71**, are formed in insignificant amounts.



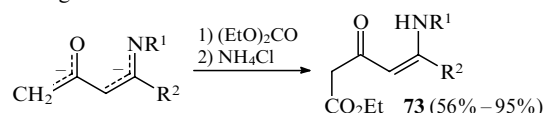
$\text{R}^1 = \text{Pr}^i, \text{Me}; \text{R}^2 = \text{Me}, \text{Et}, \text{Ph}, \text{Pr}; \text{R}^3 = \text{Me}, \text{Et}, \text{C}(\text{Me})=\text{CH}_2.$

The AVK derivatives **72** with a carboxy group in the α' -position were obtained by the reaction of the α' -dianions **53** with carbon dioxide.⁵⁵ For $\text{R}^1 \neq \text{H}$, the acids **72** are unstable and undergo decarboxylation within several hours to give the starting AVK. For $\text{R}^1 = \text{H}$, the acids **72** retain their stability at lowered temperatures over a period of several months. The dianions of the type **54** do not react with carbon dioxide.⁵⁵



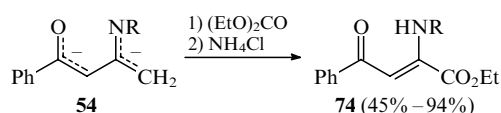
$\text{R}^1 = \text{H}, \text{Me}, \text{Et}, \text{Bn}; \text{R}^2 = \text{Me}, \text{Pr}^i, \text{Ph}, \text{cyclo-C}_7\text{H}_{12};$
 $\text{R}^3 = \text{Me}, \text{Ph}(\text{CH}_2)_2.$

The α' -dianions of the type **53** react with diethyl carbonate to give enamino oxo acids **73**.⁵⁵ The maximum yields of compounds **72** and **73** were obtained for compounds with bulky substituents at the nitrogen atom.⁵⁵



$\text{R}^1 = \text{Me}, \text{Pr}^i, \text{Ph}; \text{R}^2 = \text{Me}, \text{Et}.$

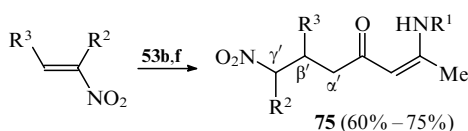
The γ -dianions of the type **54** react with diethyl carbonate to produce α -amino- β -benzoylacrylates **74**.⁵⁵



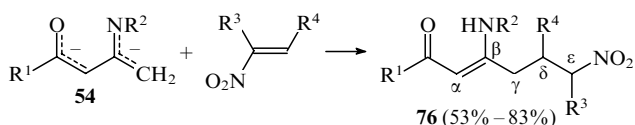
$\text{R} = \text{Me}, \text{Pr}^i, \text{Ph}.$

It is noteworthy that the condensation of $(\text{EtO})_2\text{CO}$ with the dianions **54** containing an aliphatic substituent instead of a phenyl substituent yields a complex mixture of products.⁵⁵

The dianions **53** and **54** add to the double bond of nitroalkenes to give γ' - (**75**) or ε -nitro- β -enamino ketones (**76**). As a rule, this reaction yields only one of the possible diastereomers.⁵⁶

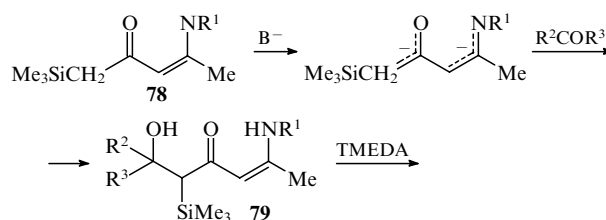


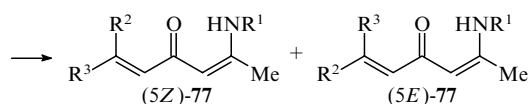
$\text{R}^1 = \text{Ph} \text{ (53f)}, \text{Pr}^i \text{ (53b)}; \text{R}^2 = \text{H}, \text{Me}; \text{R}^3 = \text{Ph}, \text{Et}, \text{Ph}(\text{CH}_2)_2, 4\text{-MeOC}_6\text{H}_4.$



$\text{R}^1 = \text{Ph}, \text{Me}; \text{R}^2 = \text{Me}, \text{Pr}^i, \text{Ph}; \text{R}^3 = \text{H}, \text{Me}; \text{R}^4 = \text{Et}, \text{Ph}, \text{Ph}(\text{CH}_2)_2, 4\text{-MeOC}_6\text{H}_4.$

The cross-conjugated enamino ketones **77** were obtained by the reaction of aldehydes and ketones with dianions formed upon treatment of α' -(trimethylsilyl)enamino ketones **78** with bases.^{57, 58}



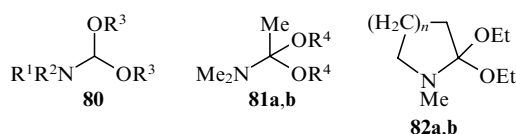


$\text{R}^1 = \text{Pr}^i, \text{Bu}^t; \text{R}^2 = \text{Ph}, \text{PhCH}=\text{CH}, \text{Et}; \text{R}^3 = \text{H}, \text{Me}.$

The structures of the products formed depend on the reaction conditions. In tetrahydrofuran, only silyl-substituted hydroxy enamino ketones **79** or their mixture with compounds **77** are isolated. In the presence of tetramethylethylenediamine which binds lithium cations and thus facilitates the elimination of trimethylsilanol only α',β' -unsaturated amino ketones **77** in a total yield of 53% to 82% are obtained. It is noteworthy that the ratios of the (5E)- to (5Z)-isomers of compounds **77** depend on the reaction time, viz., the (5Z)-isomer is mainly formed upon elimination after 2 h, whereas the (5Z)-isomer is isomerised into the (5E)-isomer with an increase in the reaction time to 20 h.⁵⁸

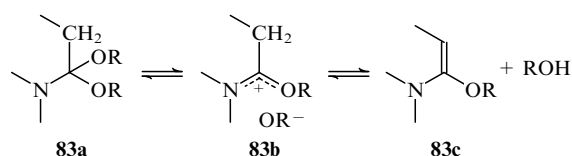
6. Reactions of amide and lactam acetals and ester amins with compounds containing an activated methylene group

Reactions of amide and lactam acetals and ester amins with compounds containing an activated methyl or methylene group is one of the most popular approaches to the synthesis of enamines including enaminoketones.^{1,59–62} Among amide and lactam acetals and ester amins synthesised to date,^{59,61–66} dialkyl acetals of *N,N*-dialkylformamides **80** and *N,N*-dimethylacetamide **81** as well as diethylacetals of *N*-methylbutyro- (**82a**) and -valerolactams (**82b**) are the most well-studied and popular synthetic reagents.



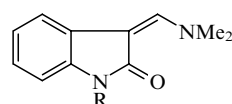
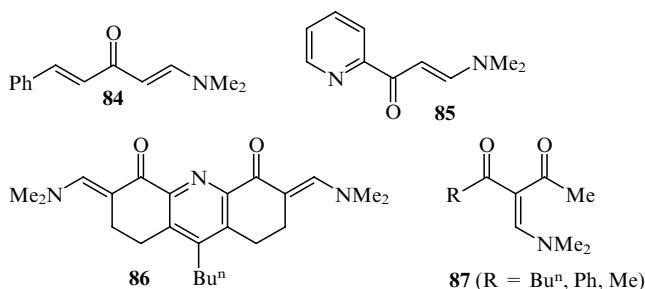
$\text{R}^1 = \text{R}^2 = \text{Et}, \text{Me}; \text{R}^1-\text{R}^2 = (\text{CH}_2)_5; \text{R}^3 = \text{Me}, \text{Et};$
 $\text{R}^4 = \text{Me}$ (**81a**), Et (**81b**); $n = 1$ (**82a**), 2 (**82b**).

In solutions of amide acetals, an equilibrium exists between acetals **83a**, ambidental cations **83b** and α -alkoxy enamines **83c**.^{66–71}



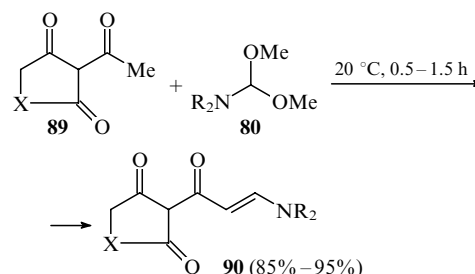
Reactions of nucleophilic substitution of amide acetals proceed in the absence of catalysts, since the abstraction of a proton from an activated methyl or methylene group occurs by virtue of the basic properties of the acetal amide itself. In some cases, azeotropic distillation may be required to remove the alcohol formed.

The condensation of dimethylformamide acetal and alkylformate amination with various ketones (e.g., aromatic, heterocyclic) and diketones gave enaminoketones **84**,⁷² **85**,⁷³ **86**,⁷⁴ **87**⁷⁵ and **88**.⁷⁶



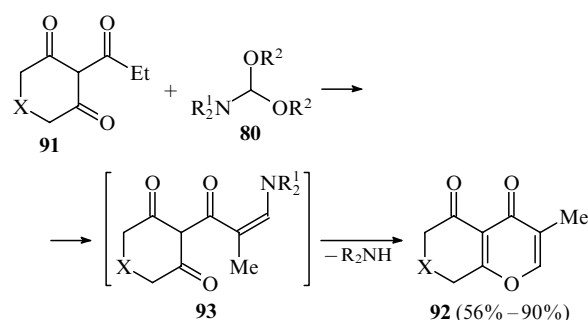
88 ($\text{R} = \text{H}, \text{Et}$).

Dialkyl acetals of *N,N*-dialkylformamides **80**^{77,78} react with 2-acetylcycloalkane-1,3-diones **89** exclusively at the acetyl group to give enaminotriketones **90**.⁷⁷



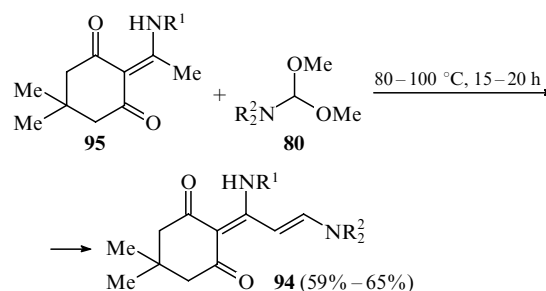
$\text{R} = \text{Me}, \text{Et}; \text{X} = \text{CH}_2, (\text{CH}_2)_2, \text{CH}_2\text{CHMe}.$

The dioxo derivatives of tetrahydrobenzopyrans **92** formed upon cyclodeamination of enaminotriketones **93** are the reaction products of 2-propionylcyclohexane-1,3-diones **91** with *N,N*-dialkylformamide acetals **80**.⁷⁸



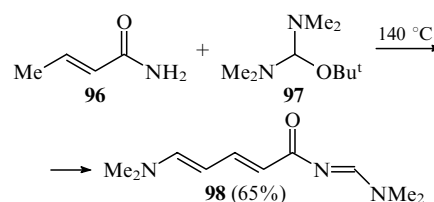
$\text{R}_2\text{N} = \text{Me}_2\text{N}, \text{Et}_2\text{N}, \text{N} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{C}_6\text{H}_4 \begin{smallmatrix} \diagdown \\ \diagup \end{smallmatrix} \text{N}; \text{R}^2 = \text{H}, \text{Me}; \text{X} = \text{CH}_2, \text{CMe}_2.$

Diaminodienediones **94** were synthesised by heating cyclic enamino β -diketones **95** with an excess of acetals **80**;⁷⁹ in this case, the reaction occurs at the methyl group which is separated from the carbonyl function by a double bond. Only few examples of this kind of reactions are documented.^{79–81}



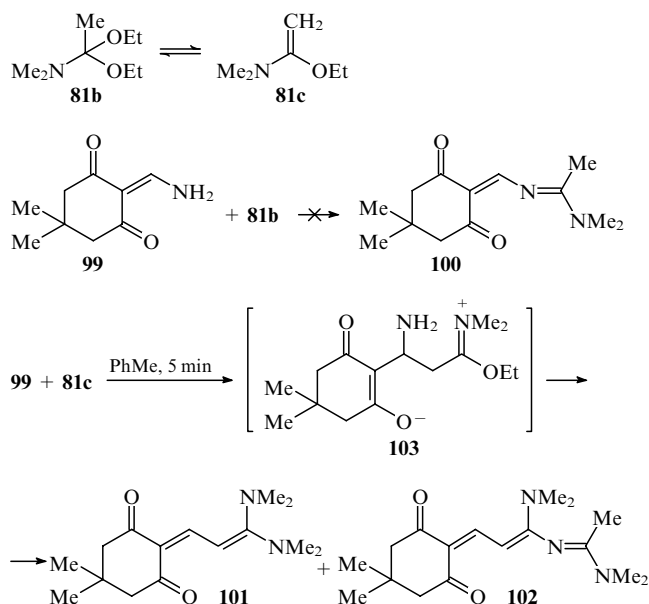
$\text{R}^1 = \text{Me}, \text{Et}; \text{R}^2 = \text{H}, \text{Me}.$

The condensation of crotonamide **96** with a large excess of *tert*-butylformate bis(*N,N*-dimethylaminal) **97** at 140 °C yields



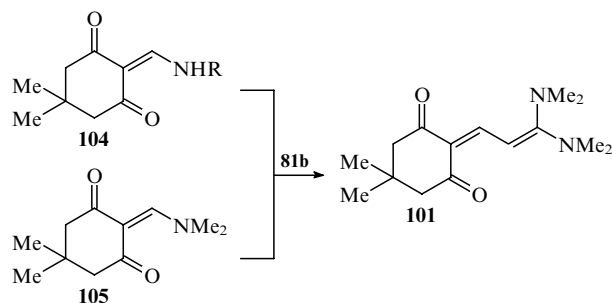
enamidines **98** as a result of reactions at both methyl and the primary amino group.⁸¹

An unusual reaction was observed in the study of the reactions of *N,N*-dimethylacetamide diethyl acetal **81b** and acetals of *N*-methylbutyro- (**82b**) and -valerolactams (**82b**) with enamino diketones. ^{1, 62, 69–71, 82} Quite unexpectedly, the reaction of the enamino diketone **99** with the acetal **81b** occurs not at the primary amino group to give enamine **100**,⁸³ but at the double bond and yields a mixture of diaminodiene diketone **101** and its dimethylaminoethylidene derivative **102**.^{1, 62, 69, 82}



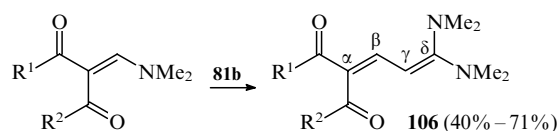
It is assumed that the reaction with enamino diketone **99** involves ketene acetal-amine **81c** rather than dimethylacetamide acetal **81b** which is in equilibrium with the former. High electron density in the β -position of ketene acetal-amine **81c**, which is provided by two strong electron-donor substituents, favours its easy addition to the double bond of the enamino diketone **99**. This results in the zwitterion **103** the alkoxy group of which reacts with dimethylamine formed in the course of the reaction to give the diaminodiene **101** or with ammonia and an excess of acetal **81b** to give amidine **102**.⁶⁹ It is clear from the scheme presented why the dimethylformamide acetals **80** for which the equilibrium of the type $\mathbf{81b} \rightleftharpoons \mathbf{81c}$ is impossible do not enter into such reactions.

Obviously, this reaction is ambiguous because of the presence of the primary amino group in the enamino diketone **99**. The introduction of *N*-substituted enamino diketones **104** and **105** into the reaction with acetal **81b** allows selective synthesis of the diamino dienediketone **101**.⁶⁹



R = Ph, Bn.

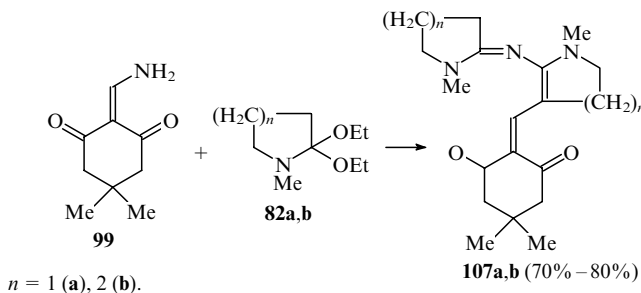
The reaction of *N,N*-dimethylacetamide acetal (**81b**) with other cyclic and acyclic enamino dicarbonyl compounds also occurs at the double bond and results in diamino dienediketones **106**.^{69, 71}



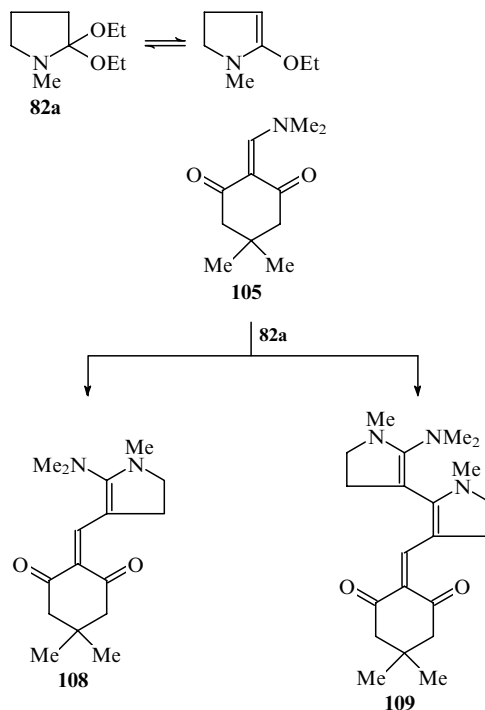
$R^1 = R^2 = \text{Me, Ph}; R^1 - R^2 = \text{OCH}_2\text{O}, (\text{CH}_2)_3$.

According to ¹H NMR spectroscopic data, δ,δ -diamino dienediones **101** and **106** exist predominantly as *s-trans*-conformers with respect to the C(β)–C(γ) bond ($J = 14.2–14.7$ Hz).

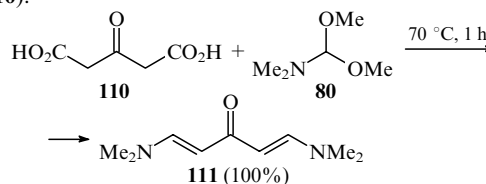
N-Methylbutyro- and -valerolactam acetals (**82a**) and (**82b**)⁷⁰ react with the enamino diketones **99** and **105** in a similar way. Thus the enamine **99** gives cyclic derivatives of dienediamines **107a,b** in high yields.⁷⁰



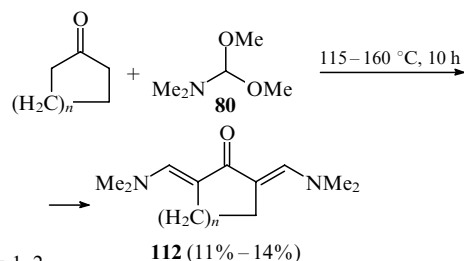
The structure of the reaction product of the lactam acetal **82a** with the enamino diketone **105** depends on the reagent ratio, *viz.*, the dihydropyrrole diene **108** is formed in the case of an equimolar ratio, whereas triene **109** is formed in the presence of an excess of the lactam acetal.⁷⁰



Dimethylformamide acetal (**80**) can also be used in the synthesis of di(β -aminovinyl) ketones.^{84–87} Thus the synthesis of 1,5-bis(dimethylamino)penta-1,4-dien-3-one (**111**) is based on the reaction of dimethylformamide acetal (**80**) with 3-oxoglutaric acid (**110**).^{84, 85}



Di(aminomethylidene)cycloalkanones **112** are formed in the reaction of dimethylformamide acetal **80** with cyclopentanone or cyclohexanone which proceeds under very drastic conditions; the yields of the target products are usually low.⁸⁶

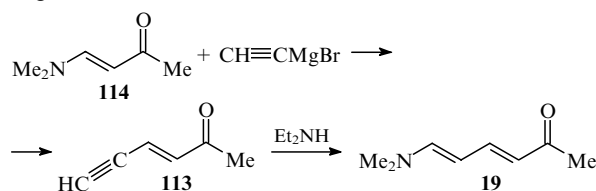


In the presence of 1,5-diazabicyclo[4.3.0]non-5-ene as a catalyst, the yields of compounds **112** increase up to 36%–50%.⁸⁷

7. Synthesis of δ -aminodienones and α, α' -bis(3-aminopropenylidene)alkanones

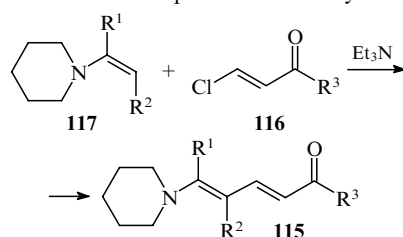
Some examples of the synthesis of δ -amino dienones were described earlier.^{88–90} In most cases, the procedures employed for the synthesis of enamino ketones are inapplicable to the synthesis of conjugated δ -amino dienones and, particularly, of polyunsaturated ω -amino ketones where the number of conjugated double bonds between the NMe₂ and CO groups is more than two.

Thus the reaction of the enynone **113** with diethylamine was used for the synthesis of δ -aminodienone **19**. The ketone **113** was synthesised from 4-dimethylaminobut-3-en-2-one (**114**) and ethynylmagnesium bromide.⁸⁸



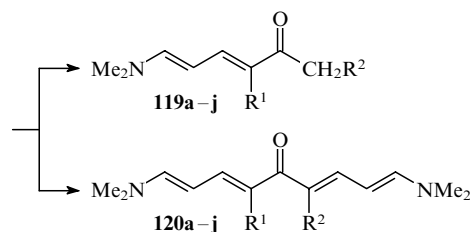
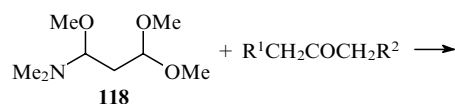
Polyunsaturated amino ketones can, in principle, be synthesised by reiteration of this procedure. However, it has been shown⁸⁹ that this approach is ineffective even in the case of trienones.

The δ -amino dienones **115** possessing aryl substituents were obtained by the reaction of aryl β -chlorovinyl ketones **116** with enamines **117** in the presence of triethylamine.⁹⁰



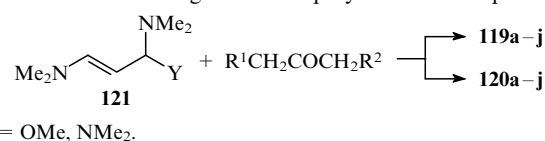
$R^1 = \text{H}, R^2 = \text{Me, Et, Ph}; R^1 - R^2 = (\text{CH}_2)_3; R^3 = \text{Ph, 4-MeC}_6\text{H}_4, 4\text{-ClC}_6\text{H}_4, 4\text{-BrC}_6\text{H}_4.$

The condensation of 3-dimethylamino-1,1,3-trimethoxypropane (**118**) (see Ref. 91) with ketones is successfully employed in the synthesis of δ -dimethylamino dienones.^{86, 92–95} Depending on the conditions, the reaction can be directed towards the formation of ketones containing one (**119a–j**) or two (**120a–j**) 3-dimethylaminopropenylidene substituents in the α -position.^{86, 92, 93, 95}



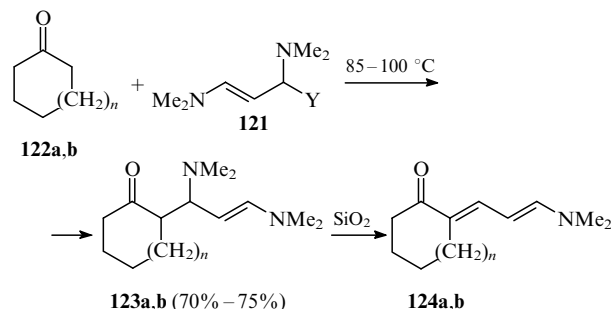
$R^1 = R^2 = \text{H}$ (**a**); $R^1 = \text{H}, R^2 = \text{Me}$ (**b**); $R^1 - R^2 = (\text{CH}_2)_2$ (**c**), $(\text{CH}_2)_3$ (**d**), $(\text{CH}_2)_4$ (**e**), $(\text{CH}_2)_2\text{CHMe}$ (**f**), $\text{CH}_2\text{CH}(\text{Me})\text{CH}_2$ (**g**), $\text{CH}_2\text{CH}(\text{Me})\text{CHMe}$ (**h**), CH_2OCHMe (**i**), CH_2OCMe_2 (**j**).

β -Dimethylaminoacrolein acetal-aminals or aminals **121** can be used for the synthesis of compounds **119** and **120** instead of 3-dimethylaminotrimethoxypropane **118**.⁹⁶ In both cases, the condensation occurs in the presence of a catalyst and virtually does not result in the formation of by-products. An important advantage of this method is the possibility to synthesise compounds **120** containing two aminopolyenoic chromophores.



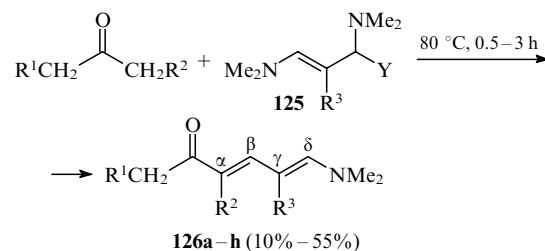
Owing to the interaction of two chromophores through the carbonyl group, the ketones **120** possess specific properties, such as pronounced solvatochromism⁹⁷ and thermochromism,⁹⁸ fluorescence and the ability to generate laser radiation with high efficiency.⁹⁹ The exceptionally easy alkylation and protonation of these compounds at the carbonyl group is accompanied by drastic changes in their colour.^{100, 101}

The reaction of β -dimethylaminoacrolein acetals or acetal-aminals **121** with cyclic ketones **122a,b** gave the intermediate compounds (diamines **123a,b**) which are quantitatively converted into α -(3-dimethylaminopropenylidene)cycloalkanones **124a,b** in CHCl_3 in the presence of SiO_2 .⁹⁴



$Y = \text{OMe, NMe}_2; n = 9$ (**a**), **12** (**b**).

The reaction of acetals or acetal-aminals **125**¹⁰² substituted in position 2 with ketones often gives only ketones **126a–h** with one 3-dimethylaminopropenylidene substituent.^{103–105}

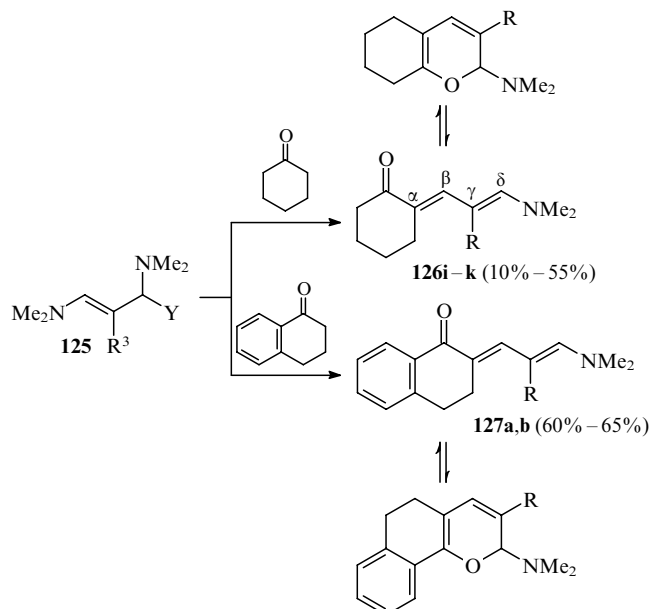


$Y = \text{OMe, NMe}_2.$

Compo- und 126	R ¹	R ²	R ³	Compo- und 126	R ¹	R ²	R ³
a	H	H	Me	e	(CH ₂) ₂		Me
b	H	H	OEt	f	(CH ₂) ₂		Cl
c	H	H	Cl	g	(CH ₂) ₂		Br
d	H	H	Br	h	(CH ₂) ₂		OEt

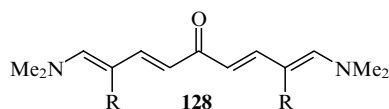
According to ¹H NMR spectroscopic data, ketone **126a** has a *trans*-configuration of the α,β -double bond ($J = 15$ Hz).¹⁰⁵ The cyclic ketones **126e–h** represent *E*-isomers with a *trans*-arrangement of the carbonyl group and a substituent in the γ -position ($^3J_{\text{CO-H}\beta} = 5.0\text{--}5.8$ Hz).^{103, 104}

In contrast to dienones **126a–h**, which exist exclusively in the open form, the γ -substituted compounds **126i–k** and **127a,b** containing a six-membered ring exist in some solvents in a dynamic equilibrium between the *Z*-isomer of the δ -amino dienone form and the corresponding 2*H*-pyran. Evidence for the existence of both forms is provided by the detection of two sets of signals in the ¹H and ¹³C NMR spectra as well as by absorption bands from both valence isomers in the UV spectra.^{103–106}

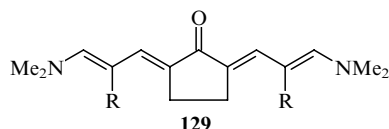


Y = NMe₂, OMe; R = Me (**126i**, **127a**), OEt (**126j**), Cl (**126k**, **127b**).

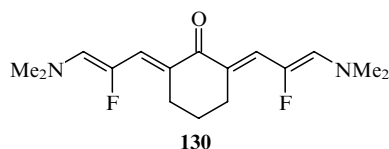
Bis(ω -dimethylamino) polyenones **128** and **129** containing Me, Ph, Cl and OEt in the γ,γ' -positions were synthesised by the reaction of the corresponding substituted acetals or acetal-aminals **125** with acetone^{107, 108} and cyclopentanone.^{103, 104, 109} Bis(3-dimethylaminopropenyldene)cyclohexanone **130** was obtained using fluorine-substituted acetals **125**.¹¹⁰



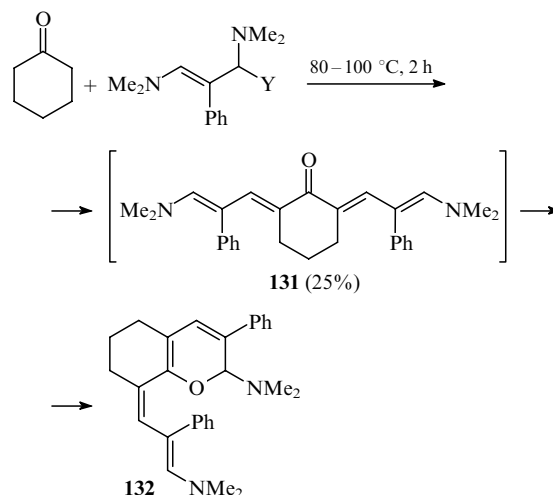
R = Me, Ph.



R = Me, OEt, Cl.

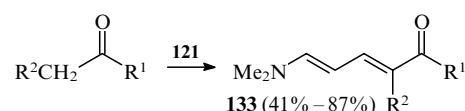


Compound **131** which is formed first was isolated in the form of its valence isomer, *viz.*, 2*H*-pyran **132**, in the reaction of α -phenyl- β -dimethylaminoacrolein acetals or acetal-aminals with cyclohexanone.¹⁰⁸



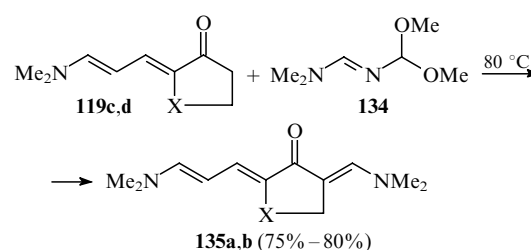
Y = OMe, NMe₂.

δ -Amino dienones **133** containing heterocyclic and heteroorganic substituents were synthesised¹¹¹ using β -dimethylaminoacrolein acetals or acetal-aminals **121**.



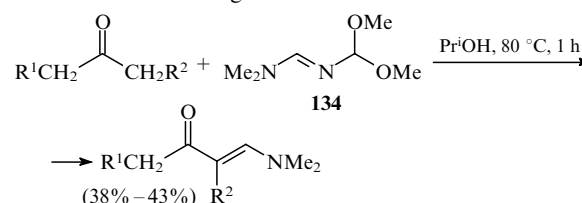
R¹ = Ph, PhCH=CH, , , , C₅H₅FeC₅H₄;
R² = H, Me, Ph.

Azaacetal **134** was used for the synthesis of unsaturated amino ketones of various structures. Thus the condensation of cycloalkanones **119c,d** with the azaacetal **134** is accompanied by the cleavage of the C=N bond resulting in non-symmetrical bis(dimethylaminoalkenyldene)alkanones **135**.¹¹²



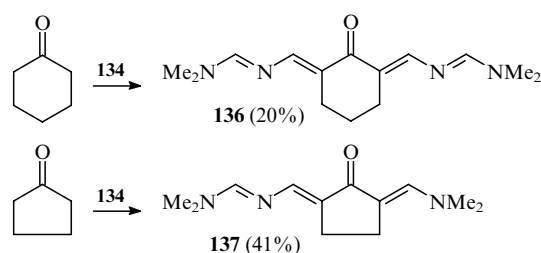
X = CH₂ (**119c**, **135a**), (CH₂)₂ (**119d**, **135b**).

The cleavage of the C=N bond also takes place in the reaction of the azaacetal **134** with cycloalkanones and acetone at an equimolar ratio of the reagents.¹¹²



R¹ = R² = H; R¹–R² = (CH₂)₂, (CH₂)₃, (CH₂)₄.

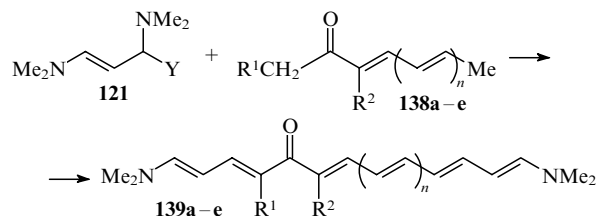
The ketones **136** and **137** containing an azamethine group were synthesised at an cycloalkanone :azaacetal **134** ratio of 1 : 2 (PrOH, 80 °C, 5 h).¹¹²



III. Conjugated ω-amino polyenones

1. Condensation of α,β-unsaturated ketones with β-dimethylaminoacrolein acetals and acetal-aminals

β-Dimethylaminoacrolein **121** acetals and acetal-aminals manifest exceptionally high reactivity. They react with cyclic and acyclic unsaturated ketones **138a,d** and their vinilologues **138b,c,e** containing no more than three double bonds at both the α-methyl (or α-methylene) group and the methyl group separated from the carbonyl function by double bonds to give bis(dimethylamino)-polyunsaturated ketones **139–141** (Scheme 1).¹¹³

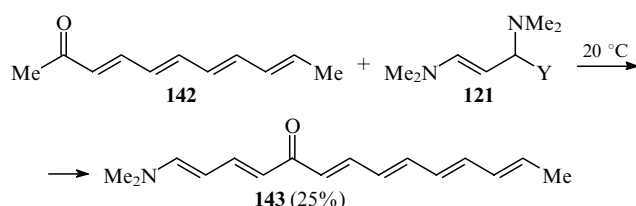


Y = NMe₂, OMe.

Compounds **138**, **139**

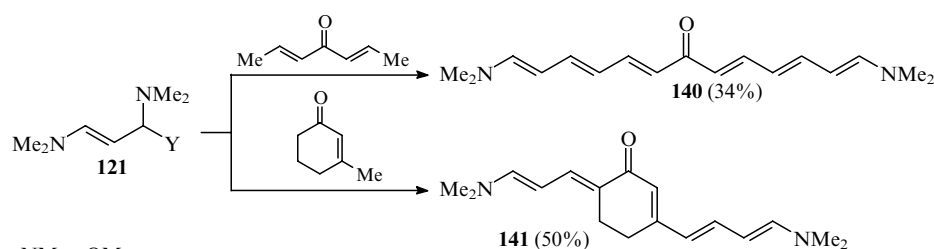
	R ¹	R ²	n	Yield of 139 (%)
a	H	H	0	54
b	H	H	1	40
c	H	H	2	27
d	(CH ₂) ₃		0	75
e	(CH ₂) ₃		1	48

In undeca-3,5,7,9-tetraen-2-one (**142**), the mobility of hydrogen atoms of the methyl group separated from the carbonyl function by four double bonds is insufficient for the condensation with compounds **121**; only the methyl group in the α-position



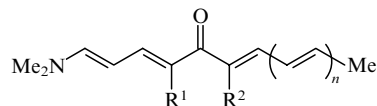
Y = NMe₂, OMe.

relative to the carbonyl group reacts to yield ketone **143** containing one 3-dimethylaminopropenyldiene group.¹¹³



Y = NMe₂, OMe.

In conjugated ketones **138a,e**, the mobility of hydrogen atoms of the methyl or methylene group vicinal to the carbonyl group is higher than that of the methyl group separated from the carbonyl group by one or several double bonds. This allows one to carry out condensation under milder conditions, *e.g.*, at equimolar ratios of reagents and without heating, which results in selective formation of reaction products involving the α-methylene group.¹¹³

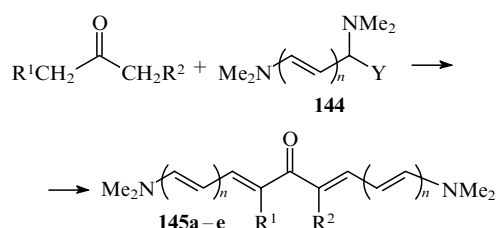


n = 0–2; R¹ = R² = H; R¹–R² = (CH₂)₃.

Unfortunately, this method is confined mainly to the synthesis of non-symmetrical polyunsaturated bis(3-dimethylaminopropenyldiene)alkanones. Moreover, this requires difficultly accessible unsaturated ketones as starting compounds.

2. Condensation of acetals and acetal-aminals of β-dimethylaminoacrolein vinilologues with ketones

The synthesis of symmetrical polyconjugated α,α'-bis(dimethylaminoalkenyldiene)alkanones is based on the use of acetals and acetal-aminals of conjugated ω-dimethylaminopolyenals **144** (n = 2, 3) which react with different ketones at both methyl or methylene groups to give bis(dimethylamino)polyunsaturated ketones **145a–e**.¹¹⁴



Y = OMe, NMe₂.

Compounds **145**

	R ¹	R ²	n	Yield of 145 (%)
a	H	H	2	98
b		(CH ₂) ₂	2	62
c		(CH ₂) ₃	2	60
d	H	H	3	3
e		(CH ₂) ₂	3	12

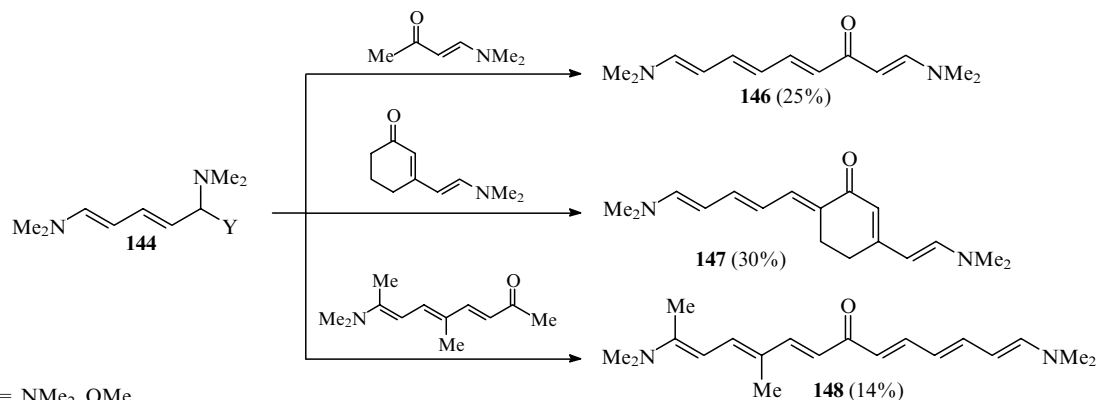
In the case of compounds **144** (where n = 3), the reaction proceeds under more drastic conditions where the polyunsaturated ketones formed are unstable. The corresponding derivatives **145d,e** could be isolated only in reactions with acetone and cyclopentanone in low yields.¹¹⁴

The condensation of acetals or acetal-aminals of δ-dimethylaminodial **144** (n = 2) with enamino, dienamino and trien-amino ketones was used for the synthesis of non-symmetrical polyunsaturated bis(dimethylamino) ketones **146–148** (Scheme 2).^{114, 115}

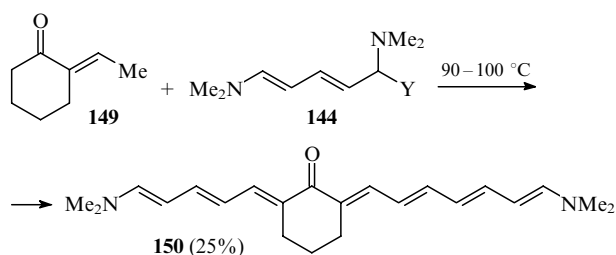
It should be noted that compounds **144** (where n = 2) are characterised by sufficiently high reactivities to react with 2-ethylidenecyclohexanone (**149**) at both the α-methylene and the methyl

Scheme 1

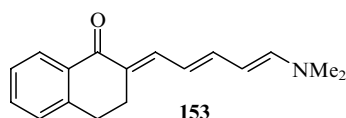
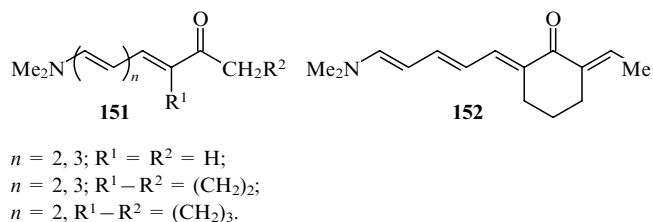
Scheme 2



group separated from the carbonyl function by a double bond to yield the derivative **150**.¹¹⁴

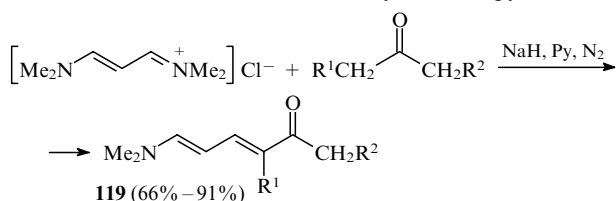


With a change in reaction conditions (*viz.*, with equimolar ratio of the reactants, gentle, short-term heating), the reaction of acetals and acetal-aminals of ω -dimethylaminopolyenals **144** with ketones occurs in a regioselective manner and yields the polyunsaturated ketones **151–153** which contain only one dimethylamino group.¹¹⁶



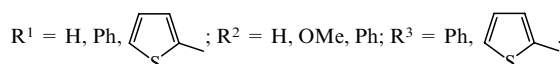
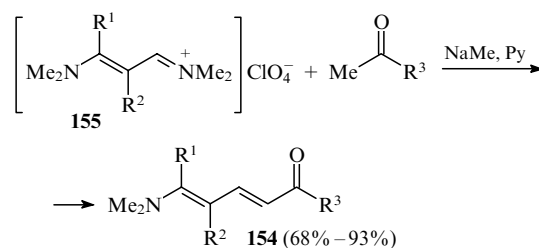
3. Condensation of ketones with polymethine salts

Yet another well-studied approach to the synthesis of ω -amino polyenones, is the condensation of ketones with trimethine or pentamethine salts in the presence of bases, such as NaNH_2 ,¹¹⁷ MeOK , MeONa or Bu^tOK ,^{87, 111, 118–120} NaH or LDA .^{121–124} As a rule, this reaction is carried out in triethylamine or pyridine.

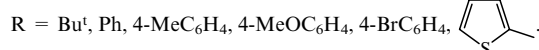
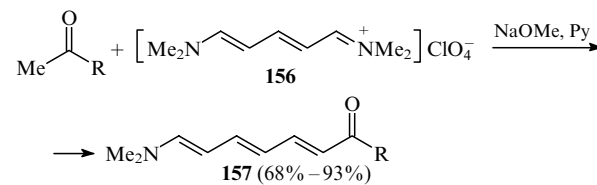


δ -Dimethylaminoalka-1,3-dienyl ketones **154** having substituents in the aminopolyene chain were prepared by the condensation

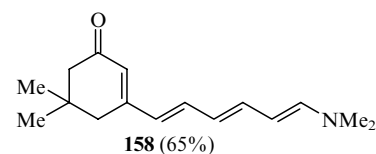
of aromatic and heteroaromatic methyl ketones with the substituted trimethine salts **155**.^{111, 118, 120}



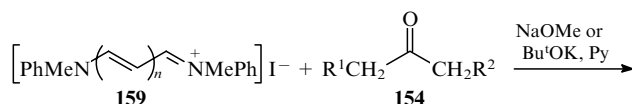
The reaction of the pentamethine salt **156** with methyl ketones makes it possible to synthesise ω -aminopolyunsaturated ketones **157** with a more extended chromophore.¹¹¹

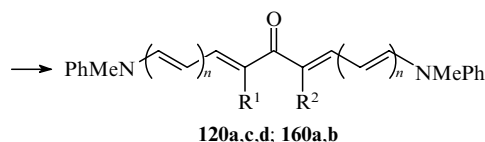


The condensation of isophorone with the pentamethine salt **156** involves the methyl group (rather than the sterically shielded α -methylene group), which affords the aminopolyunsaturated ketone **158** where NMe_2 and CO groups are separated by four double bonds.¹¹¹



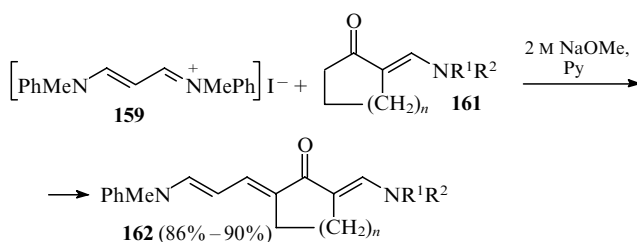
The reaction of tri- and pentamethine salts **159** with ketones in pyridine in the presence of MeONa (2 equiv.) or Bu^tOK was used¹¹⁹ to obtain the symmetrical diamino polyenones **120a,c,d** and **160a,b**. The yields of ξ -dimethylamino trienones **160a,b** do not exceed 35%.





Compounds	R ¹	R ²	n	Yield (%)
120a	H	H	1	55
120c	(CH ₂) ₂		1	83
120d	(CH ₂) ₃		1	65
160a	(CH ₂) ₂		2	26
160b	(CH ₂) ₃		2	35

The non-symmetrical cyclic polyunsaturated ketones **162** were prepared from cyclic enamino ketones **161**.⁸⁷

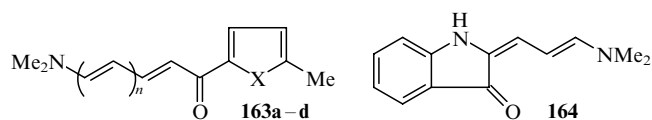


R¹ = H, Me; R² = Ph, Me.

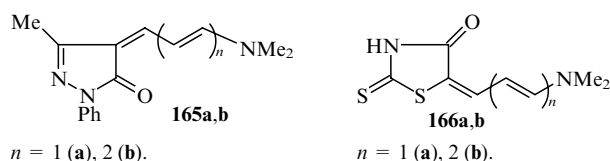
IV. Conjugated ω-amino ketones containing a heterocyclic fragment

The synthesis of conjugated ω-amino ketones containing a heterocyclic fragment which strongly affects their physicochemical properties has been carried out in the last few years.

Thus the condensation of heterocyclic ketones containing an acetyl or an activated methylene group with acetals and acetal-aminals **121** or **144a,b** was used to obtain δ-amino dienones **163a**,¹¹³ **164**, **165a**, **166a**,¹⁰⁹ **167a**, **168a**¹²⁵ and ξ-amino trienones **163b**, **165b**, **166b**, **167b**, **168b**¹²⁵ and **169**¹¹⁶ containing a heterocyclic fragment.

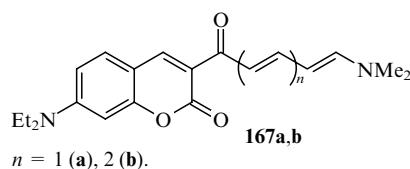


X = O, S; n = 1 (**a**), 2 (**b**);
X = O; n = 2 (**c**), 3 (**d**).

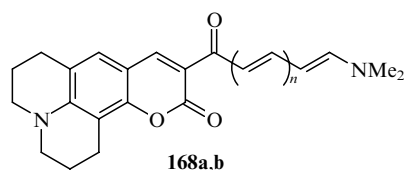


n = 1 (**a**), 2 (**b**).

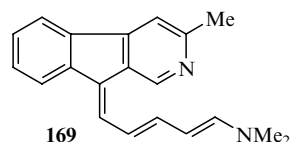
n = 1 (**a**), 2 (**b**).



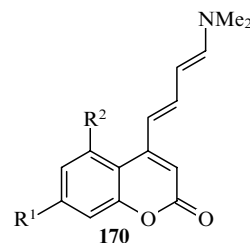
n = 1 (**a**), 2 (**b**).



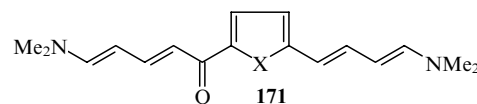
n = 1 (**a**), 2 (**b**).



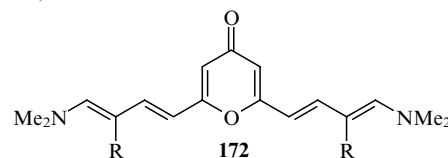
High reactivities of compounds **121** enable their reactions with the methyl group separated from the carbonyl group by a double bond or by a heterocyclic fragment to give the ω-amino polyenones **170–172**.^{113, 125, 126}



R¹ = Me, OH; R² = H, OMe.



X = O, S.



R = H, Me, Ph.

* * *

In conclusion, it may be said that the ω-amino polyenones **168**, **169** and **170** containing a coumarin fragment are very valuable, since coumarin derivatives constitute an important group of organic luminophores and laser dyes which effectively generate radiation in the region of 400–560 nm.^{127, 128} In addition, they are widely employed in medicine and biochemistry as fluorescent compounds.¹²⁹ 2,6-Bis(4-dimethylaminoalka-1,3-dienyl)-4H-pyran-4-ones (**172**) appeared to be very interesting reagents from the spectral and synthetic standpoints.¹²⁶

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Optical spectra and photophysical properties of polychlorinated dibenzo-*p*-dioxin derivatives

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Abstract. Published data on the optical spectra and theoretical investigations of dioxins, polychlorinated derivatives of dibenzo-*p*-dioxin, which are well-known environmental toxins, are generalised. The geometrical and electronic structures of the molecules and their vibrational and electronically excited states are considered. The influence of the number and positions of chlorine atoms in dioxin molecules on the optical spectra (IR and UV absorption, fluorescence and phosphorescence spectra), in particular, on the low-temperature fine-structure phosphorescence spectra of solid solutions and on the photophysical deactivation of triplet electronic states are discussed. The results of the use of optical spectroscopy for identification and quantification of dioxins are presented. The bibliography includes 108 references.

I. Introduction

Compounds of the dibenzo-*p*-dioxin series, also called dioxins, became widely known and fell into disrepute after high toxicity of some polychlorinated dibenzo-*p*-dioxins (PCDD) had been established.^{1–5} Due to their high stability, dioxins formed in industrial processes can be retained in soil and water for long periods, enter living organisms and be accumulated in them. Due to the extreme hazard of dioxin ecotoxins, investigation of their physicochemical properties and development of highly sensitive methods for their detection and quantification have become urgent.

Several reviews devoted to the methods and results of determination of PCDD in environmental objects and biological tissues have been published;^{6–10} however, they mainly discuss the data of GC/MS methods of analysis, while the data of spectroscopic studies used for analytical purposes are scanty. Since the mid-1980s, the physicochemical properties of PCDD have been studied more vigorously, in particular, by spectroscopic methods. These methods possess a great analytical potential; they can be used to identify various PCDD in different media and to perform quantitative analysis. Furthermore, spectroscopic meth-

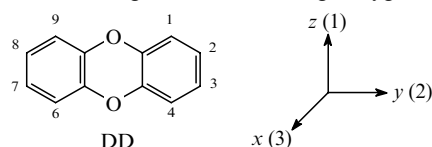
ods can also be used to solve a fundamental problem, namely, to elucidate the relationship between the structures and physicochemical properties of PCDD molecules. They provide valuable information about the interaction of the molecule with light, its steric and electronic structure, various types of intra- and intermolecular interactions, *etc.* With the progress in elucidation of the structure and physicochemical properties of PCDD, the mechanism of toxic action and the pathways of deactivation of these toxins would gradually become clear.

The present review is, in our opinion, the first attempt to survey the published data obtained by both experimental and theoretical methods of optical spectroscopy on the structure, vibrational and electronic states of dioxin molecules and the physicochemical properties of dioxins. Data from IR, Raman, electronic absorption, fluorescence and phosphorescence spectra are discussed, in particular, fine-structure electronic-vibrational (vibronic) phosphorescence spectra at temperatures of 77 and 4.2 K are presented. The manifestation of vibronic and vibronic-spin-orbit couplings in the fine structure of vibronic spectra, the change of the nuclear configuration of molecules in the triplet excited state, the rate constants of radiative deactivation of singlet and triplet electronic states, and the effect of the number and the positions of chlorine atoms in the PCDD molecule on the phosphorescence spectra and the phosphorescence rate constants are discussed. The last Section contains the results of the use of optical spectra (UV and IR absorption, fluorescence, phosphorescence) for identification of dioxins and determination of their quantity.

II. Molecular and electronic structure of dioxins

1. Molecular structure

Dibenzo-*p*-dioxin (DD) is an aromatic cyclic ether consisting of two benzene rings connected through oxygen bridges.



X-Ray diffraction data for DD^{11–13} and for five of its chloro-derivatives [mono-, di-, tetra-, hexa-, and octachlorodioxins (OCDD)]^{14–19} have been described in the literature. In the crystals, the dioxin molecules are nearly planar, although some atoms including Cl atoms deflect from the plane. Thus in di-¹⁶ and

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hexachlorodioxin molecules,¹⁷ the angle between the C—Cl bond and the plane amounts to 3–4°, while in mono-,^{14, 16} octa-^{16, 18} and tetrachlorodioxins,^{15, 16, 19} this angle does not exceed 2°. The C—Cl bond length in mono-, di- and hexachlorodioxin molecules varies from 1.69 to 1.75 Å. The geometric parameters of the central fragment of the molecules differ insignificantly: the C—O bond length is equal to 1.36–1.38 Å and the angle between the C—O bonds (δ_{COC}) is $\sim 116^\circ$. Thus, the size of the COC angle in dioxins is intermediate between those in anisole (110°) and diphenyl oxide (120°).²⁰

According to X-ray diffraction data, the central fragment of dioxin molecules can be considered to be planar. In the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (β -TCDD),[†] the oxygen atoms deflect slightly from the plane through the four carbon atoms in different directions, thus forming a 'chair' configuration of the central fragment.¹⁶ However, the angle of deflection is only 0.8° . In the DD molecule,¹¹ all six atoms of the central fragment lie in one plane but this plane as a whole is somewhat (by 0.5°) rotated around axis 1. The C—O bond length in dibenzo-*p*-dioxin is 1.383 Å, the internal and external CCO angles are 122° and 118° , and the central COC angle is 116° . Note that the geometric parameters determined from X-ray diffraction data refer to molecules forming the crystal lattice. No experimental data for these parameters in free dioxin molecules have been reported in the literature.

In several studies, the geometric structures of dioxins have been determined theoretically, the geometry being optimised using semiempirical²¹ and *ab initio*^{22, 23} calculations. According to some data,^{21, 22} the DD and β -TCDD molecules are planar and the calculated values of bond lengths and angles are close to those found experimentally.¹⁵ According to another publication,²³ the DD molecule is non-planar: the benzene rings are rotated with respect to the axis which passes through oxygen atoms (axis *z*) to form a dihedral angle equal to 167.93° (subsequently, this molecular configuration is called a 'butterfly'). According to a calculation²³ carried out in the same approximation, the cation derived from the DD molecule is planar in the ground electronic state.

In an earlier publication,²¹ DD has also been suggested to have a 'butterfly' configuration. Thus the dipole moment of a solution of DD in benzene was found to be 0.55 D (rather than zero). The molecule was modelled as the 'butterfly' configuration and the dihedral angle was estimated from the dipole moment. It was found to be 164° . Note that this conclusion cannot be regarded as unambiguous because the molecule could acquire a dipole moment due to interaction with the solvent without losing planarity; for example, it could occur as a configuration with C_{2v} symmetry with retention of the $C_2(z)$ symmetry axis.

The problem of the structure of dioxins attracts attention because the toxicity of PCDD is supposed to be correlated with either planar or non-planar structure of their molecules.²⁴ Grainger *et al.*²⁴ proposed determination of the molecular configuration on the basis of the δ_{COC} angle: if this angle is 109 – 111° , the molecular is non-planar. For some PCDD, the COC angles were found²⁴ using approximate calculation procedures based on a triatomic model and using spectroscopic data on the frequency of the stretching antisymmetrical vibrations of C—O—C groups. It was concluded that the PCDD molecule becomes more planar as the number of α -chlorine atoms decreases. However, this conclusion should be treated critically because the triatomic model is too rough to provide an adequate description of the vibrations of a polyatomic molecule.

The authors of most spectroscopic studies of dioxins give preference to the planar configuration, relying on the experimental data on molecular geometry; however, some researchers decide in favour of the 'butterfly'.

[†] In considering the spectral properties of polyaromatic derivatives, for example, substituted naphthalenes, anthracenes, 9,10-anthraquinones and so on, the positions of substituents are designated by Greek letters.

The highest-symmetry group to which planar dioxin molecules can belong is the D_{2h} group (this group of symmetry corresponds to the planar molecules of DD, β -TCDD, 1,4,6,9-Cl₄DD and OCDD). A molecule with the 'butterfly' configuration has C_{2v} symmetry in which the following symmetry elements are retained: the $C_2(x)$ axis and two symmetry planes σ_1 and σ_2 , perpendicular to the Cartesian coordinates *z* and *y*, respectively. The $C_{2v}(D_{2h})$ groups of symmetry are matched by the following correlation of irreversible representations:

$$A_1(A_g + B_{3u}), B_2(B_{2u} + B_{1g}), B_1(B_{1u} + B_{2g}), A_2(B_{3g} + A_u). \quad (1)$$

To answer the question about the configuration of the dioxin molecules mentioned above, it is expedient to use correlation (1) and employ selection rules when analysing spectroscopic data (see Sections III and IV).

2. Electronic structure of molecules

The ground electronic state (S_0) of the planar DD molecule is characterised by the following charges (ρ_e) on the atoms of the central fragment, oxygen and four carbons: $\rho_e(\text{O}) \approx -0.37$ and $\rho_e(\text{C}) \approx +0.22$ (in the electron charge units) on each of equivalent atoms. The calculation was carried out by the INDO/S semi-empirical approximation. The charges on the C—H group atoms are small in magnitude (~ 0.05 – 0.09 units) and have opposite signs (for carbon $\rho_e < 0$).

The presence of four Cl atoms in the planar β -TCDD molecule does not change the charge distribution in the central fragment with respect to that in DD. Charge redistribution in β -TCDD takes place on the atoms of the C—Cl groups — the negative charge on each chlorine atom [$\rho_e(\text{Cl}) \approx -0.12$] reverses the sign of the charge on the corresponding β -carbon atoms [$\rho_e(\text{C}) \approx +0.11$]. The changes in the charge on the C—H group atoms are reduced to a slight increase in their magnitude ρ_e (to ~ 0.08 – 0.12), their signs being retained. The same pattern of charge distribution is observed for OCDD: $\rho_e(\text{O}) \approx -0.34$, $\rho_e(\text{C}) \approx +0.20$ in the central fragment, while for C—Cl groups with the chlorine atoms in the α - and β -positions $\rho_e(\text{Cl}) \approx -(0.09$ – $0.10)$ and $\rho_e(\text{C}) \approx +(0.07$ – $0.09)$.

Thus, an increase in the number of Cl atoms in dioxin molecules (from zero to eight) barely influences the charge distribution on the atoms of the central six-membered fragment of the molecules in the ground electronic state S_0 . A theoretical study²⁵ of the electron-donating properties of DD, β -TCDD and 1,4,6,9-Cl₄DD molecules has also demonstrated that the π -donor properties of these molecules (as well as their geometric structure) depend only slightly on the positions of Cl atoms.

An important characteristic of the ground electronic state S_0 of a molecule is the ionisation potential (IP). The first IP for several dioxin molecules (DD, 2-ClDD, 2,8-Cl₂DD) cooled in a supersonic jet of argon were determined experimentally by the resonance-enhanced two-colour two-photon ionisation technique.^{23, 26} For nine dioxins containing zero to eight chlorine atoms in the molecule, a semiempirical calculation²³ of the IP values in the Koopmans approximation was performed. It was found that, as the number of chlorine atoms in the molecule increases, the IP value increases monotonically by approximately 0.1 eV for each additional Cl atom. Indeed, the IP for DD, β -TCDD and OCDD are 7.58, 7.99 and 8.42 eV, respectively. It is of interest that the pattern of dependence of the IP on the number of Cl atoms in dioxins differs substantially from that observed in the series of chloro-substituted benzene derivatives in which the number of Cl atoms ranges from zero to six.^{23, 27} In the case of chlorobenzenes, the IP value barely changes upon an increase in the number of Cl atoms (9.25 and 9.19 eV for benzene and hexachlorobenzene, respectively). This difference between the patterns of IP variation for these series of compounds was attributed²³ to the presence of oxygen in dioxin molecules.

According to the Koopmans approximation, the IP values are determined by the energy of the highest occupied molecular orbital (with allowance for an adjusting parameter selected

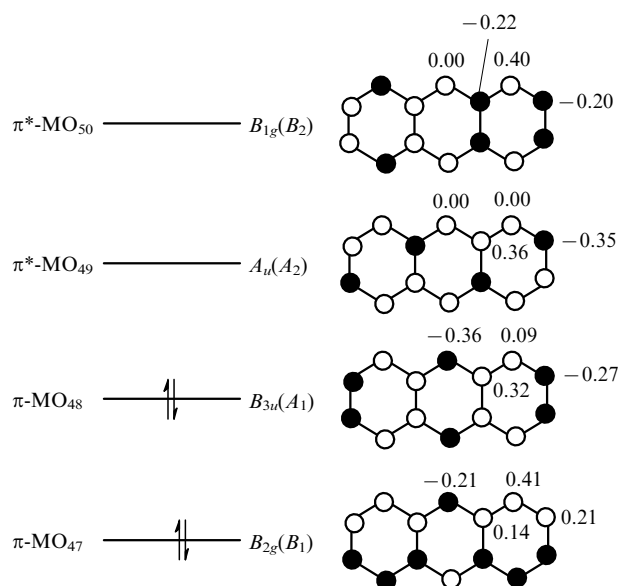


Figure 1. Classification of four MO of the DD molecule according to irreducible representations of the $D_{2h}(C_{2v})$ groups and their representation as a LCAO. The numerical values for the coefficients²⁸ at the $2p_x$ -AO are given; the dark and light circles correspond to different signs of the coefficients at these AO.²³

empirically for a particular series of molecules, for example, for dioxins²³). Figure 1 shows a π -MO (MO_{48}) of the DD molecule for which the 'butterfly' configuration has been accepted.²³ From representation of the structure of this MO_{48} as a linear combination of atomic orbitals (AO), one can see that the oxygen atoms can actually affect substantially the IP in the DD molecule.

In connection with the results of studies of the dioxin IP, it is of interest to mention the data obtained in the calculations of the electronic states in the planar dioxin molecules^{28,29} concerning the influence of Cl atoms on the structure of the highest occupied π -MO (MO_{48}), which determines the theoretical IP value. It was found that for this MO, the coefficients at the $2p_x$ -AO centered at the O and C atoms in the β -TCDD and OCDD molecules with D_{2h} symmetry differ only slightly (by hundredths of a unit) from the corresponding values for the DD molecule (see MO_{48} in Fig. 1). For OCDD, the coefficients at the $2p_x$ -AO of the chlorine atoms proved to be relatively low: +0.13 for β -Cl and -0.03 for α -Cl. Since the coefficients at the $2p_x$ -AO of oxygen for DD, β -TCDD and OCDD do not depend (with an accuracy of < 3%) on the number of chlorine atoms in the molecule, in our opinion, the difference between the patterns of variation of IP in chlorobenzenes and dioxins can hardly be definitely attributed to the influence of the O atoms, as has been proposed in a publication.²³

Figure 1 also shows characteristics of a lower occupied MO_{47} , the removal of an electron from which²³ transforms the DD molecule into a cation, as well as characteristics of the vacant MO_{49} and MO_{50} . The electronic configurations corresponding to the transition of an electron from MO_{48} to MO_{50} and from MO_{47} to MO_{49} determine the properties mainly of the lower singlet electronically excited state S_1 having $B_2(B_{2u})$ symmetry. This is a resonance state in two-photon two-colour resonance-enhanced ionisation experiments.²³ Analysis of the signs of the coefficients at $2p_x$ -AO (see Fig. 1) centred on the atoms of the C—O—C groups for four MO led the researchers to the conclusion²³ that the DD molecule has different configurations in different electronic states. For instance, on passing from the S_0 state with a 'butterfly' configuration to the cationic form or to the S_1 state, the DD molecule is believed to become flatter, due to the increase in the bond orders in these states. However, the arguments presented in the study in question²³ seem inconclusive. The spectroscopic data concerning the problem of the configuration of the DD molecule

in different electronic states (S_0 and S_1) are presented in Section IV.

III. Vibrational states

1. Experimental data

The molecules of dioxins contain 22 atoms and have 60 normal modes. In planar molecules, 41 modes are in-plane vibrations and 19 modes are out-of-plane vibrations. In the infrared, Raman, fluorescence and phosphorescence spectra, which display the vibrations of molecules in the ground electronic state, only vibrations with particular types of symmetry can be observed, depending on the symmetry of the molecule, in accordance with the selection rules.

In molecules with D_{2h} symmetry, vibrations are classified into eight representations (types of symmetry) of this group:

$$11A_g + 10B_{3g} + 10B_{1u} + 10B_{2u} + 4B_{1g} + 5B_{2g} + 5A_u + 5B_{3u}.$$

The last four types are out-of-plane vibrations (which normally correspond to frequencies of < 1000 cm^{-1}). Vibrations with g type of symmetry are active in the Raman spectra, while u -type vibrations (except for A_u) are IR active. The vibrations active in the phosphorescence spectra are totally symmetric A_g and non-totally symmetric vibrations of either g or u type, depending on the type of symmetry of the electronically excited state. Of the set of non-totally symmetric vibrations, out-of-plane vibrations are usually responsible for the most intense lines in the $\pi\pi^*$ phosphorescence spectra of heteroaromatic compounds³⁰ (it is these spectra that are typical of dioxins).

Thus, in order to gain exhaustive information concerning the vibrations of dioxin molecules with a symmetry higher than C_s , various spectroscopic methods should be used. Meanwhile, IR spectra of dioxins have been studied most extensively due to the necessity of identifying these hazardous compounds.

The molecules of chlorinated dioxins contain heavy Cl atoms; the frequencies of the fundamental vibrations of these molecules vary²² over a broad range, ~ 3300 – 20 cm^{-1} . However, as a rule, the IR spectra of dioxins are measured^{2,24,31–37} in a narrower frequency range, namely, above 800 cm^{-1} . Data on the IR vibration frequencies of PCDD molecules in KBr pellets,^{2,31} in the gas phase,^{24,34} and under conditions of matrix isolation (argon matrix at 12 K)^{33,35–37} have been reported. In particular, the spectra of 22 isomers of tetrachloro-substituted DD in an argon matrix and in the vapour phase were recorded.³³

The attention was focused on the IR spectra of the most toxic β -TCDD.^{2,32–34} The IR spectrum of this compound in a KBr pellet was measured² in a wider frequency range (4000–375 cm^{-1}) than the spectra of other tetrachloro-substituted DD. Figure 2 shows a fragment of this spectrum.³⁷

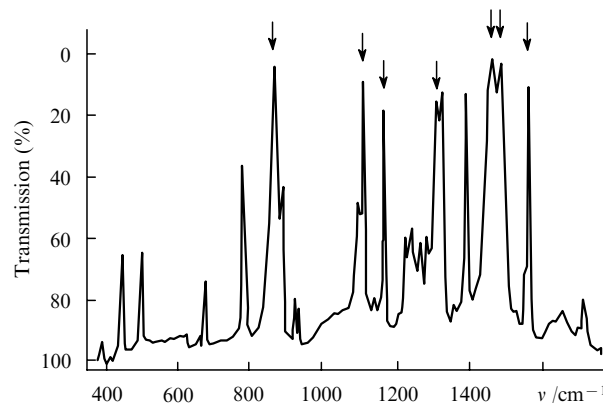


Figure 2. IR absorption spectrum of β -TCDD in a KBr pellet.² The arrows mark the spectral regions in which analytical lines were identified in a study with matrix isolation.³⁷

The researchers were especially interested in the fact^{22,34} that the IR spectra of tetrachloro-substituted DD recorded under various experimental conditions exhibited doublet splitting of some lines. In the case of β -TCDD, this splitting is observed in the region of 1480, 1315 and 1115 cm^{-1} (see Fig. 2). The results of a theoretical study of the possible causes of this effect in β -TCDD gave rise to the conclusion²² that Fermi resonance is the main reason.

If the molecular configuration of any dioxin has an inversion centre, only about a half of the fundamental modes are displayed in the IR spectra, while the other frequencies are active in the Raman spectra. The most comprehensive IR and Raman data have been reported for DD^{38,39} and OCDD⁴⁰ (Raman spectra of OCDD are shown in Fig. 3). For other PCDD, to the best of our knowledge, no data on the Raman spectra are available.

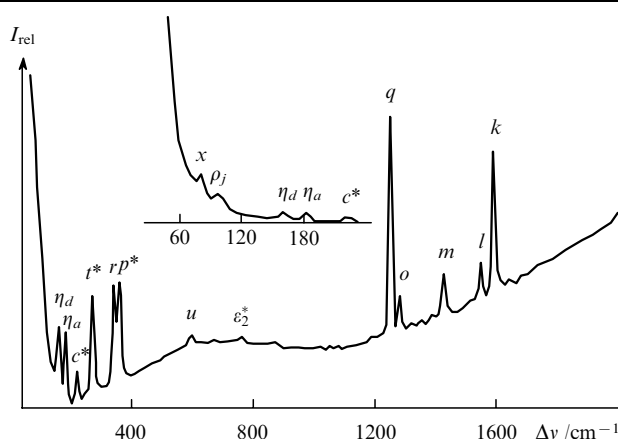


Figure 3. Raman spectrum of the OCDD powder, $\lambda_{\text{excit}} = 488 \text{ nm}$.⁴⁰ The spectral lines are marked by the letter designations of vibrations used in Tables 1 and 2. The asterisk marks the vibration frequencies for which a different interpretation is possible (see Table 4).

The frequencies of the fundamental modes of the molecules of some dioxins [DD, β -TCDD, 1,3,6,8-tetrachlorodibenzo-*p*-dioxin (α,β -TCDD), OCDD] in the ground electronic state were also determined by analysis of the fine-structure phosphorescence spectra^{39,41–43} (the results of analysis of these spectra are outlined in Section V). For DD, 2,7-Cl₂DD, 2,8-Cl₂DD and 2,3-Cl₂DD molecules cooled in a supersonic jet, the vibrational structure of the first singlet electronically excited (S_1) state was obtained using the resonance two-photon ionisation method.^{23,26,44–46}

On the basis of a study of the IR spectra, an empirical interpretation of a number of absorption bands of dioxins has been proposed.^{2,24,31,37} As an example, we cite the empirical interpretation of seven frequencies corresponding to the analytical lines in the β -TCDD spectrum (see Fig. 2):³⁷ 1575, 1489, 1471 cm^{-1} are skeletal in-plane vibrations of the C=C groups in the aromatic fragments; 1312 cm^{-1} is an antisymmetric stretching vibration of the C–O–C groups; 1176 and 1117 cm^{-1} are in-plane deformation and stretching (breathing) vibrations of the aromatic fragments; and 879 cm^{-1} is an out-of-plane vibration of the C–H groups. Studies of the vibrations of dioxins resorting to the data of theoretical calculations^{22,39–41} have shown that this assignment has to be corrected.

2. Calculation and interpretation of vibrations

The calculations for vibrations in the harmonic approximation were performed with the assumption of a planar configuration of the molecule. For several tetrachloro-substituted DD isomers (β -TCDD, 1,4,6,9-Cl₄DD, 1,3,7,8-Cl₄DD, 1,4,7,8-Cl₄DD)²² and a number of hepta- and hexa-chloro-substituted PCDD isomers,⁴⁷ an *ab initio* quantum-chemical calculation of vibrations was performed using scaling factors. For a number of molecules

having the same D_{2h} symmetry but different numbers of chlorine atoms, DD, β -TCDD and OCDD, the normal modes were calculated^{39–41} by the classical method.⁴⁸ When applying this method to dioxins, the potential field of a molecule with a similar structure (xanthone) was chosen as the base.^{49,50} As the hydrogen atoms were replaced by chlorine atoms, the increments³⁹ corresponding to the force constants of the C–C(Cl)–C groups in chlorinated benzenes were introduced without variations. Scaling factors for some natural vibrational coordinates of related molecules were used in the *ab initio* calculation;^{22,51} for PCDD, they were not varied either.

The results of calculations were used to determine the frequencies of all the normal modes of the dioxins studied;^{22,39–41} an interpretation for each vibration was proposed.

In view of the fact that each vibration of the molecule usually has a complex form (combination of the amplitudes of variation of all bond lengths and bond angles in the molecule), different approaches to the interpretation have been proposed;^{50,51} they were presented, for example, in Refs 22 and 40. One approach⁵¹ makes use of the results of calculations of the distribution of the total energy of vibrations over atomic groups. In this case, each calculated vibration frequency in dioxins²² is usually matched to vibrations of several atomic groups. For instance, the intense band with a maximum at about 1480 cm^{-1} (see Fig. 2) in the IR spectrum of β -TCDD was assigned²² to the skeletal vibrations of the aromatic fragments and the deformation vibrations of the CH groups in the plane of the molecule. In another approach,⁵⁰ for each calculated normal mode of dioxins,⁴⁰ data on the local type of symmetry were taken into account [within the framework of the D_{6h} (D_{2h}) groups of symmetry for the movement of atoms in the separate six-membered fragment of the molecule⁵⁰], in addition to the relative vibration amplitudes of separate groups of atoms (Table 1). In Table 1, the vibration modes were assigned to the vibrations of particular atomic groups – the benzene fragment

Table 1. Letter designations⁴⁰ of the vibrations of dioxins and their assignment.

Designation of vibrations ^a	Atomic group
In-plane vibrations	
$k [e_{2g}(a_g)], l [e_{2g}(b_{3g})], m [e_{1u}(b_{1u})], n [e_{1u}(b_{2u})], o [b_{2u}(b_{2u})], r [a_{1g}(a_g)]$	C=C stretching (BF)
$p [b_{1u}(b_{1u})], s [e_{2g}(b_{3g})], t [e_{2g}(a_g)]$	CCC deformation (BF)
$q (a_g), q (b_{2u}), z (b_{3g}), z (b_{1u})$	CO stretching (CF)
$u (a_g), c (b_{1u}), c (b_{3g})$	COC, OCC deformation (CF)
$a [b_{2u}(b_{2u})], b [e_{1u}(b_{1u})], d [e_{1u}(b_{2u})], e [a_{2g}(b_{3g})]$	CCH deformation ^b
ε	CCl stretching
η	CCCl deformation ^c
Out-of-plane (deformation) vibrations	
$v [b_{2g}(b_{2g})], y [e_{2u}(b_{3u})], \omega [e_{2u}(a_u)]$	CCCC (BF)
$f [e_{2u}(b_{3u})], g [a_{2u}(b_{3u})], i [e_{1g}(b_{2g})], j [b_{2g}(b_{2g})]$	CH ^b
ρ	CCl ^c
$\chi (b_{2g}), \chi (b_{3u})$	CCOC (CF)
$x (b_{1g}), x (b_{3u}), h (a_u)$	BF + CF ^d

Note. BF and CF are the benzene and central fragments.

^a The local types of symmetry [$\Gamma(\Gamma')$] of the D_{6h} (D_{2h}) point group are given in brackets.

^b For terminal atomic groups, the designation [$\Gamma(\Gamma')$] has a meaning if all their four atoms in a fragment are identical.

^c For C–Cl groups, subscripts can be added to the designations η and ρ corresponding to the letter designations for the C–H groups (to provide a more detailed interpretation of vibrations) if the fragment contains four chlorine atoms.

^d Vibrations of the benzene fragments mutual with respect to one another.

(local symmetry D_{6h}) and the central fragment (local symmetry D_{2h}) and to vibrations of the terminal (C–H and C–Cl) atomic groups. A more detailed interpretation of vibrations according to their form⁴⁰ was performed taking into account the definite alternation of the signs of the amplitudes characterising the changes in the bond lengths and angles in the given molecular fragment; this characteristic is reflected in a definite local (for each fragment) type of symmetry of the $D_{6h}(D_{2h})$ point group. This type of analysis of the forms of vibrations makes it possible to distinguish between normal modes assigned roughly to the same atomic groups (for example, to six-membered carbon fragments). This individual form of a normal mode of dioxin was designated by a special letter symbol (in particular, the known Whiffen designations of the vibrations of benzene and monosubstituted benzene derivatives were used).

Tables 2–5 contain the calculated values for all the vibration frequencies^{22,40} in the DD, β -TCDD and OCDD molecules distributed over types of symmetry of the D_{2h} point group, together with the corresponding experimental values found from vibrational spectra (IR and Raman) or fine-structure phosphorescence spectra. In the case of β -TCDD, the calculated vibration frequencies determined by different methods^{22,40} are in fairly good agreement; however, the use of different methods for the

Table 2. Frequencies of the in-plane vibrations of the DD and PCDD molecules calculated theoretically and obtained experimentally from the Raman and phosphorescence spectra.

Designations of vibrations	ν_{DD} (R) ^a	$\nu_{\beta\text{-TCDD}}$ (phos) ^{a, b}	$\nu_{\beta\text{-TCDD}}$ ^c	ν_{OCDD} (R) ^a
Vibrations of A_g symmetry				
<i>k</i>	1602 (1621)	1586 (1600)	1595	1566 (1590)
<i>n</i>	1470 (1500)	1449 (1442)	1483	1346
<i>o</i>	1310	1296 (1284)	1296	1281 (1280)
<i>q</i>	1208 (1226)	1222 (1236)	1226	1256 (1250)
<i>a</i>	1152 (1154)	1119 (1100)	1111	
ε_1				898
ε_2		662 (654)	661	733 (754*)
<i>d</i>	1023 (1030)			
<i>r</i>	735 (726)	745 (739)	741	325 (345)
<i>t</i>	613 (564)	232 (206)	254	242 (274*)
<i>u</i>	363 (398)	586 (548)	555	601 (594)
η_d		167 (149)	183	146 (162)
η_a				169 (181)
Vibrations of B_{3g} symmetry				
<i>l</i>	1610 (1586)	1596	1574	1578 (1550)
<i>m</i>	1452	1380	1358	1392 (1425)
<i>z</i>	1317	1209	1154	1218
<i>e</i>	1254 (1192)	1263	1218	
<i>b</i>	1112 (1094)			
ε_3				730
ε_4		972 (985)	986	974
<i>p</i>	883 (898*)	595	538	324 (358*)
<i>s</i>	547 (534)	637 (628*)	642	525
<i>c</i>	477 (450*)	236	227	198 (220*)
η_b		383 (383*)	391	162
η_e				786

Note. From here on, vibration frequencies are given in cm^{-1} ; experimental vibration frequencies determined from Raman (R) or IR and phosphorescence (phos) spectra are given in parentheses. The asterisks mark the unambiguous assignments of frequencies to in-plane or out-of-plane vibrations. The Table does not contain the stretching vibrations of the C–H groups. The pairs of designations ε_1 , ε_2 or ε_3 , ε_4 imply different signs of the amplitudes of the changes in the C–Cl bond lengths in each BF.

^a From the data of Ref. 40. ^b From the data of Ref. 39. ^c From the data of Ref. 22.

Table 3. Frequencies of the in-plane vibrations of DD and PCDD molecules calculated theoretically and found experimentally from IR spectra.

Designations of vibrations	ν_{DD} ^a	$\nu_{\beta\text{-TCDD}}$ ^{a, b}	$\nu_{\beta\text{-TCDD}}$ ^c	ν_{OCDD} ^a
Vibrations of B_{2u} symmetry				
<i>k</i>	1584 (1590)	1564 (1568)	1557	1543 (1550)
<i>n</i>	1466 (1495)	1446 (1456)	1470	1366 (1390)
<i>o</i>	1279 (1300)	1271 (1312)	1269	1256 (1298)
<i>q</i>	1293 (1395)	1290 (1326)	1303	1279 (1320)
<i>a</i>	1151 (1154)			
ε_1				813 (840)
ε_2		1106 (1114)	1107	979 (987)
<i>d</i>	1023 (1030)	864 (876)	870	
<i>r</i>	827 (830)	432 (450)	445	452
<i>t</i>	598 (610)	680 (680)	686	308
η_d				203
η_a		177	198	168
Vibrations of B_{1u} symmetry				
<i>l</i>	1622 (1628)	1610	1629	1594
<i>m</i>	1457 (1462)	1345 (1393)	1387	1388 (1423)
<i>z</i>	1196 (1200)	1186 (1172)	1170	1194 (1196)
<i>e</i>	1327 (1305)	1267 (1242)	1234	
<i>b</i>	1147 (1120)			
ε_3		914 (876)	930	864 (850)
ε_4				996 (1003)
<i>p</i>	883 (854)	834 (789)	786	443
<i>s</i>	676	303	326	332
<i>c</i>	245	119	111	83
η_b		512 (500*)	497	178
η_e				699 (666)

^a According to Ref. 40. ^b According to Ref. 39. ^c According to Ref. 22.

analysis of the forms of vibrations^{50,51} precludes a proper comparison of various approaches to the interpretation.

It is worth noting that the approach⁵⁰ taking into account the local symmetry of vibrations (unlike that described in Refs 22 and 51) allows correlation of the vibrations of molecules which belong

Table 4. Frequencies of the out-of-plane vibrations of DD and PCDD molecules calculated theoretically and found experimentally from Raman or phosphorescence spectra.

Designations of vibrations	ν_{DD} (R) ^a	$\nu_{\beta\text{-TCDD}}$ (phos) ^{a, b}	$\nu_{\beta\text{-TCDD}}$ ^c	ν_{OCDD} (R) ^a
Vibrations of B_{2g} symmetry				
<i>j</i>	977	890	846	
<i>i</i>	861 (898*)			
ρ_i		115	110	358
ρ_j				85 (97)
χ	533	600 (628*)	610	601
<i>v</i>	725 (748)	730	648	754 (754*)
ω	258 (278)	309	277	199 (220*)
Vibrations of B_{1g} symmetry				
<i>f</i>	943	895 (867)	874	
<i>g</i>	744 (764)			
ρ_g		322 (383*)	372	140
ρ_f				323 (274*)
<i>y</i>	430 (450*)	435 (441)	437	570
<i>x</i>	223 (242)	119	134	67 (80)

^a According to Ref. 40. ^b According to Ref. 39. ^c According to Ref. 22.

Table 5. Frequencies of the out-of-plane vibrations of DD and PCDD molecules calculated theoretically and found experimentally from IR spectra.

Designations of vibrations	ν_{DD}^a	$\nu_{\beta\text{-TCDD}}^{a,b}$	$\nu_{\beta\text{-TCDD}}^c$	ν_{OCDD}^a
Vibrations of A_u symmetry				
j	977	891	845	
i	861			
ρ_i		228	216	334
ρ_j				91
v	741	744	629	767
ω	521	599	610	602
h	144	55	48	38
Vibrations of B_{3u} symmetry				
f	945 (922)	899 (890)	875	
g	750 (743)			
ρ_g		205	168	89
ρ_f				213
χ	511 (450)	515 (500*)	444	606
y	357	403 (390)	383	449
x	70	33	19	31

^a According to Ref. 40. ^b According to Ref. 39. ^c According to Ref. 22.

to different point groups of symmetry. For example, this approach was used to perform a correlation of all the vibrations in mono-, di- and tetrachloro-substituted 9,10-anthraquinones.⁵² In addition, in experimental and theoretical studies of the vibrations of the DD and β -TCDD molecules as well as 9,10-anthraquinone and tetra- β -chloro-substituted 9,10-anthraquinone molecules, it has been established that the frequencies and forms of vibrations for these molecules are very close.³⁹ Therefore, interpretation of the vibrations of chlorinated 9,10-anthraquinones, which are more readily available, can be taken as the base for the investigation of the corresponding dioxins.⁵²

The variation of frequencies of all 60 vibrations following an increase in the number of Cl atoms in the series of DD, β -TCDD and OCDD, the molecules of which correspond to the same group of symmetry D_{2h} , was discussed in detail.⁴⁰ We shall briefly note some regularities⁴⁰ of the variation of the frequencies of vibrations with the same form in the DD, β -TCDD and OCDD molecules.

In-plane vibrations. The high-frequency in-plane vibrations of the carbon skeleton (in the range of 1650–1200 cm^{-1}), which can be assigned to the k , l , m , n , o stretching modes (of the benzene fragments) and q , z stretching modes (of the central fragment), change insignificantly, on the average by 5%, as the H atoms are replaced by Cl atoms (see Tables 2, 3). In the case of the two other stretching vibrations (A_g and B_{2u}) of the benzene fragments, designated by r (which should be matched to the only totally symmetric vibration r of the core of benzene molecule in the region of 995 cm^{-1}), the vibration frequencies found for DD and OCDD differ appreciably, by a factor of about two. Note that the vibrations r are characterised by low frequencies also in other molecules with benzene side fragments, even when they contain no heavy atoms.⁵⁰ For example,⁵³ in anthracene $\nu_r = 753$ (A_g) and 808 cm^{-1} (B_{2u}).

The frequencies of all [except for one, s (B_{3g})] low-frequency deformation vibrations of the carbon skeleton of the molecule (p , s , t , c , u) also change substantially, by approximately 200–300 cm^{-1} (by up to 65%), when all the H atoms have been replaced by Cl atoms. The stretching vibrations of the C–Cl (ϵ) groups of the OCDD molecule were matched to frequencies in the region of 1000–750 cm^{-1} .

In many studies, considerable attention is devoted to the identification of the IR bands caused by the presence of the

C–O ether groups in the molecules.²⁰ For example, in the case of diphenyl oxide, which contains a C–O–C group, the frequency $\nu_{C-O}^{as} = 1236$ cm^{-1} was assigned to antisymmetric stretching vibrations of this group. In molecules with D_{2h} symmetry, the q (B_{2u}) and z (B_{3g}) modes can be matched to these vibrations (see Tables 2, 3). In various PCDD, frequencies in the region of 1330–1280 cm^{-1} were attributed to an antisymmetric vibration. It is noteworthy that the vibration frequencies of the C–C groups in the anthracene molecule with the rigid six-membered central fragment are close to the vibration frequencies of the C–O ether groups in DD. The frequencies (in cm^{-1}) of the stretching vibrations of the C–O or C–C groups of the central fragment of DD, 9,10-anthraquinone and anthracene are presented below for comparison.^{50, 53}

	DD	9,10-Anthraquinone	Anthracene
A_g	1226	1148	1260
B_{3g}	1317	1284	1376
B_{1u}	1200	1335	1274
B_{2u}	1395	1173	1398

In the DD molecule, as in other molecules having a similar structure and containing eight H atoms in the benzene fragments, each of the eight in-plane deformation vibrations of the C–C–H groups belongs to a particular frequency region (see Tables 2, 3), namely, 1360–1240 cm^{-1} (e are high-frequency vibrations) and 1150–1000 cm^{-1} (a , b , d is a group of relatively low-frequency vibrations). For similar deformation vibrations of the C–C–Cl (η) groups of the OCDD molecule, two appreciably different frequency regions can also be distinguished. The range of 800–700 cm^{-1} is typical of the analogues of the vibrations e , while 200–150 cm^{-1} is the range where the analogues of the vibrations a , b and d show themselves.

The empirical interpretation of the spectrum does not always coincide with the interpretation based on calculations. Below we present the assignment of vibrations according to their form based on the use of the local types of symmetry for several vibration frequencies of the β -TCDD molecule, which differs from the empirical assignment (presented at the end of Section III.1).³⁷ Thus the frequency of 1312 cm^{-1} (B_{2u}) refers to the vibration o of the benzene fragments (with the local type of symmetry b_{2u}); 1172 (B_{1u}) and 1114 cm^{-1} (B_{2u}) correspond to the stretching vibrations z of the central fragment and ϵ of the C–Cl groups, respectively. A frequency of 450 cm^{-1} was assigned to the ‘breathing vibration’ r of the benzene molecules (the vibration B_{2u} with the local symmetry a_{1g}), while a frequency of 1326 cm^{-1} was attributed to the antisymmetric vibration of the C–O–C groups.

Out-of-plane vibrations. The main distinctive feature of most of the 11 out-of-plane vibrations of the carbon skeleton of the DD, β -TCDD and OCDD molecules is that their frequencies increase rather than decrease upon an increase in the number of Cl atoms in the molecule (see Tables 4, 5). Indeed, in the region above 300 cm^{-1} , the frequencies of only two, the highest-frequency out-of-plane vibrations of OCDD (of the v type, assigned to the benzene fragments) change relatively slightly (by 3%–4%) with respect to the frequencies of the same vibrations in β -TCDD and DD. The other vibration frequencies increase appreciably, by 13%–33%, which implies displacement of the bands in the spectrum by 70–140 cm^{-1} .

A different pattern of variation is observed for the other four lower-frequency vibrations of the molecular skeleton (below 300 cm^{-1}), namely, one vibration ω , which was assigned to the benzene moieties, and three vibrations x and h , assigned to the central moiety. These frequencies, conversely, tend to decrease (by 25% to 75%).

It should be mentioned that the vibrations x and h can be related to the rotations of two benzene fragments with respect to one another (Fig. 4). The molecule thus assumes a ‘butterfly’ (x , B_{3u}), ‘chair’ (x , B_{1g}) or ‘propeller’ (h , A_u) configuration. For comparison, Fig. 4 shows the form of the high-frequency out-of-

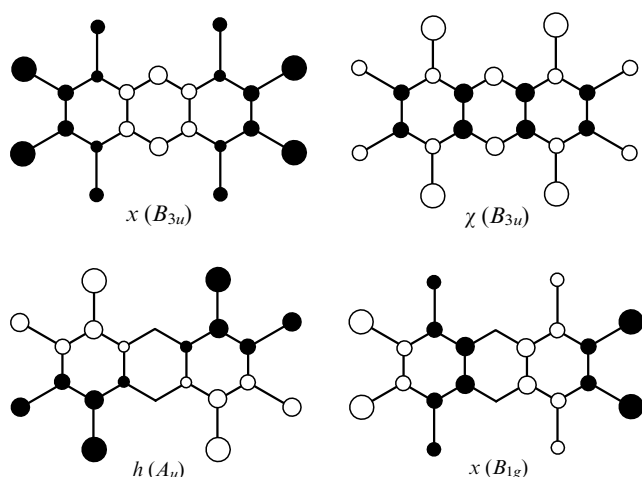


Figure 4. Forms of some out-of-plane vibrations of the DD molecule of D_{2h} symmetry (for vibration frequencies, see Tables 4, 5). The signs and the magnitudes of the displacements of atoms with respect to the plane of the molecule are marked by circles of different sizes and colours.

plane vibration $\chi (B_{3u})$. It can be seen that both x and χ vibrations of the B_{3u} type can be attributed to the molecule in the 'butterfly' configuration but x is related to a larger extent to the rotations of the benzene fragments and χ is related to the shifts of oxygen atoms.

The four out-of-plane vibrations of the C–Cl groups (ρ) of the β -TCDD molecule show themselves at low frequencies, about ~ 100 , 215 and 320 cm^{-1} . An increase in the number of chlorine atoms does not result in any significant increase in the frequency range for the eight vibrations ρ of the OCDD molecule; these vibrations remain in approximately the same frequency regions: ~ 90 – 140 , ~ 215 and $\sim 360\text{ cm}^{-1}$.

Note that the eight out-of-plane vibrations of the C–C–H groups in DD, like those in other molecules having a similar structure and containing eight H atoms in the benzene fragments, correspond to a definite frequency region: 980 – 940 cm^{-1} (j, f), $\sim 860\text{ cm}^{-1}$ (i), 750 – 680 cm^{-1} (g). However, it was found that similar vibrations of the C–C–Cl groups (ρ with the corresponding subscripts) of the OCDD molecule cannot be matched successively to higher or lower frequencies (see Tables 4, 5). For example, both ρ_j and ρ_g vibrations in OCDD are characterised by low frequencies.

Molecular configuration. To decide between the planar and non-planar ('butterfly') configurations of the DD and OCDD molecules, we shall consider the structure of their Raman spectra taking into account the selection rules for the D_{2h} and C_{2v} groups of symmetry and the correlation of their irreducible representations (1). If the molecule has the 'butterfly' configuration, *i.e.* belongs to the C_{2v} symmetry group, all the vibrations should be active in the Raman spectra, including the u -type vibrations, which are forbidden in the case of the D_{2h} group [see expression (1)]. In particular, the out-of-plane B_{3u} vibrations of the D_{2h} group become totally symmetric. The results of interpretation of the Raman spectra of two dioxins, DD and OCDD, demonstrate that all lines in the spectra of these compounds can be assigned to g -type vibrations, which implies a planar configuration of the molecule (see Fig. 3, Tables 2, 4).

IV. Singlet electronically excited states

1. Experimental data

Dioxins, like most benzene derivatives, are colourless, *i.e.* they do not absorb light in the visible region. The UV absorption spectra of dioxins [$S_m(\pi\pi^*) \leftarrow S_0$] have been studied in solution^{2, 54–57} and in the vapour phase.⁵⁸ Tables listing the absorption maxima

and the molar extinction coefficients (ϵ_{max}) have been reported;² the absorption curves for DD and its chloro-derivatives (β -TCDD, 1,2,3,7,8-Cl₅DD and OCDD) can be found in several publications.^{55, 56, 58}

The absorption spectra of DD and PCDD occur in the region of 200–350 nm and consist of two bands — a weak broad long-wavelength band (**A**) in the region of 280–320 nm with a maximum at ~ 300 – 304 nm and a short-wavelength narrow intense band (**B**) with a maximum at about ~ 220 – 240 nm . It can be seen from the absorption curves of some dioxins^{56, 58} that the high-frequency absorption band has one more, even shorter-wavelength maximum (**C**); for example, in the spectra of solutions of DD, it is separated from band **B** by $\sim 5.5\text{ nm}$.⁵⁵ As examples, Figs 5 and 6 show the absorption spectra of a solution of DD and of the β -TCDD vapour.

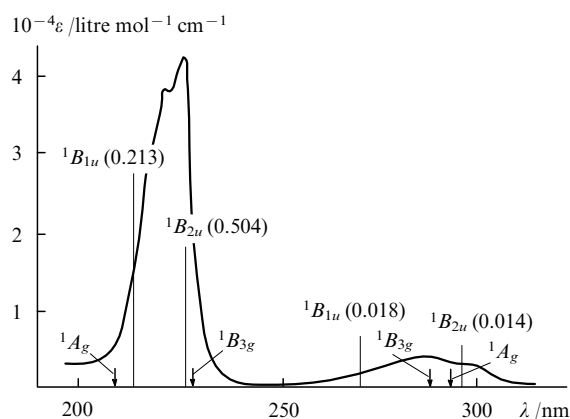


Figure 5. Electronic absorption spectrum of a solution of DD in isopentane at 77 K⁵⁶ and results of a quantum-chemical calculation²⁹ (vertical lines) of the energy and the type of symmetry of electronic $\pi\pi^*$ states and the oscillator strengths of transitions (given in parentheses). Dipole-inactive transitions are marked by arrows. The calculated spectrum as a whole is shifted by $\sim 5000\text{ cm}^{-1}$ to lower frequencies.

The ratio of the molar extinction coefficients of bands **B** and **A**, ϵ_B/ϵ_A , for solutions of DD in isopentane⁵⁶ is equal to ~ 10 , while for β -TCDD and OCDD vapours,⁵⁸ $\epsilon_B/\epsilon_A = 9$ and 35. In particular,⁵⁸ for OCDD, $\epsilon_A = 0.05 \times 10^4$ and $\epsilon_B = 1.73 \times 10^4\text{ litre mol}^{-1}\text{ cm}^{-1}$.

It should be noted that the data on the molar extinction coefficients are presented in few publications and, moreover, the reported ϵ values are not always close in magnitude. For example, for DD in isopentane,⁵⁷ chloroform² and heptane,²¹ $\epsilon_A = 0.37 \times 10^4$, 0.37×10^4 and $0.74 \times 10^4\text{ litre mol}^{-1}\text{ cm}^{-1}$; for β -TCDD in chloroform² and in the vapour phase,⁵⁸ $\epsilon_A = 0.56$ and $0.41 \times 10^4\text{ litre mol}^{-1}\text{ cm}^{-1}$. The ϵ_A values reported for vapour and for chloroform solutions of OCDD^{2, 58} differ by a factor of five. These differences may be due to both the interaction of dioxins with a solvent and the error in the determination of the true concentration of dioxins in the samples studied.

The spectra of chloroform solutions of DD and several PCDD² showed an unusual intensity ratio of the absorption bands, namely, the short-wavelength band **B** was found to be less intense than band **A**. For example, $\epsilon_B/\epsilon_A = 0.28$, 0.53 and 5.5 for DD, β -TCDD and OCDD [for comparison, for DD in isopentane, $\epsilon_B/\epsilon_A \approx 10$ (see Ref. 56)]. In our opinion, this effect is caused by the disturbing influence of the solvent, which also absorbs in the short-wavelength region of the spectrum ($< 240\text{ nm}$).⁵⁹

The absorption properties of DD are similar to those of other aromatic ethers. The spectra of ethers usually contain two absorption bands; the long-wavelength band with $\epsilon \approx (0.16$ – $0.3) \times 10^4\text{ litre mol}^{-1}\text{ cm}^{-1}$ is located at about

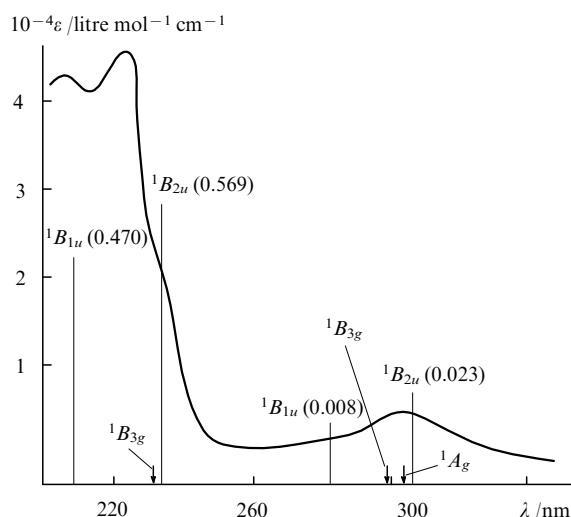


Figure 6. Electronic absorption spectrum of β -TCDD vapours⁵⁸ and the results of a quantum-chemical calculation²⁹ of the energy and type of symmetry of electronic $\pi\pi^*$ states and the oscillator strengths of transitions. For designations, see Fig. 5.

250–290 nm and the short-wavelength band with $\epsilon \approx (0.8–1.8) \times 10^4$ litre mol⁻¹ cm⁻¹ occurs in the region of 210–240 nm.²⁰ Both bands are associated with transitions from the electronic states corresponding to the benzene chromophore perturbed by the heteroatom of the ether group.

As the number of chlorine atoms in dioxin molecules increases from zero to eight, the long-wavelength band in the absorption spectra of solutions shifts bathochromically.² Thus in the spectra of chloroform solutions of DD, β -TCDD and OCDD, bands A are responsible for maxima at 293, 310 and 318 nm. However, in the case of vapours, the positions of the maxima of bands A and B virtually do not change — in the series β -TCDD, 1,2,3,7,8-Cl₅DD and OCDD, band A has a maximum at about 303–305 nm, while the maximum of band B is at ~ 223 nm.⁵⁸

In the UV absorption spectra of DD in isopentane recorded at 77 K, the long-wavelength band has several maxima,⁵⁶ which can be attributed to the vibrational structure. The vibrational fine structure of the electronically excited state S_1 for the DD, 2,7-Cl₂DD, 2,8-Cl₂DD and β -TCDD molecules was obtained using the method of resonance-enhanced two-photon ionisation in a supersonic argon jet.^{44–46} The vibrational structure of the S_1 state of the DD molecule²³ is shown in Fig. 7. In this type of spectrum of any dioxin, the first (lowest-frequency) line was assigned to the purely electronic transition $S_1 \leftarrow S_0$. As a result, the following energies of the S_1 state were determined for these dioxins:²³ 33774 (DD), 32805 (2,7-Cl₂DD), 32729 (2,8-Cl₂DD) and 32100 cm⁻¹ (β -TCDD). These frequencies are shifted by ~ 750 cm⁻¹ to shorter wavelengths²³ with respect to those in the spectra of iso-octane solutions.

The fine structure of the spectra of the $S_1 \leftarrow S_0$ electronic transition has not been interpreted yet. It should be noted that the results of full interpretation of the spectra performed for many other molecules are widely used, for example, to determine the symmetry of the first electronically excited state, to study the mechanisms of intramolecular interactions, to decide between the retention and the change of the symmetry of the nuclear configuration of the molecule upon transition from the ground state to the electronically excited state and to gain quantitative data concerning the change in the geometrical parameters of the molecule in the electronically excited state. Some results of the interpretation of the spectra of dioxins for the lower triplet state are presented in Section V.

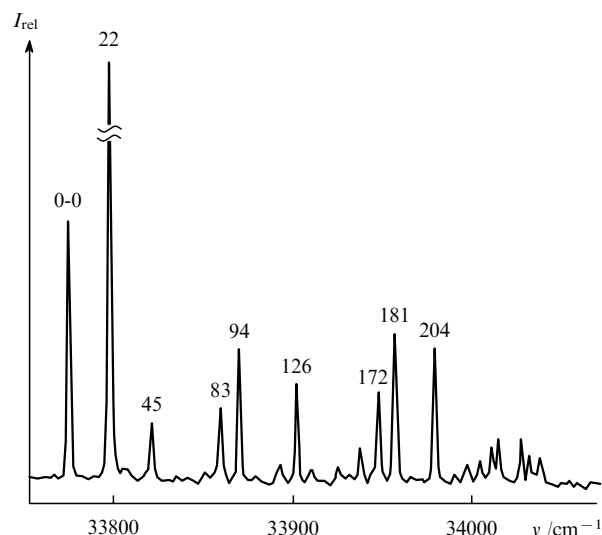


Figure 7. Vibrational structure of the electronically excited state S_1 ($\pi\pi^*$) of DD molecules cooled in a supersonic jet of argon recorded using resonance-enhanced two-photon ionisation.²³

The spectrum shown in Fig. 7 has prompted several conclusions²³ (which we consider erroneous) concerning the nuclear configurations of this molecule in the ground and in the S_1 electronic states. For example, the most intense line of this spectrum (vibration frequency 22 cm⁻¹) was assigned²³ to a ‘butterfly’ type vibration in the electronically excited state S_1 [the form and the frequency of this vibration, $\chi(B_{3u})$, in the ground electronic state are presented in Fig. 4 and in Tables 4, 5). Since this spectrum contained numerous low-frequency lines and the researchers found it to be similar to the corresponding spectrum of dihydroanthracene,⁶⁰ they²³ arrived at the conclusion that the configurations of the DD molecule in the S_1 and S_0 states are different. It was concluded that the molecule has a ‘butterfly’ configuration in the S_0 state and becomes flatter in the S_1 state. However, this conclusion appears doubtful. Indeed, the ratio of the intensities of the strong and weak lines in the spectrum of DD (see Fig. 7) can be distorted due to the known saturation effect.⁶¹ In addition, the strong line, assigned to a ‘butterfly’ type vibration, does not form an intense progression (unlike that in the spectrum of the dihydroanthracene molecule): the lines corresponding to the frequencies 22×2 , 22×3 , etc., are either weak or missing. Meanwhile, it is intense lines due to vibration overtones in the electronic-vibrational spectra that normally point to a change in the nuclear configuration of the molecule.^{62, 63}

2. Calculation of the electronic states

In order to interpret the observed electronic spectra of several dioxins (DD, β -TCDD, α,β -TCDD and OCDD), semiempirical calculations for electronically excited states have been carried out in the PPP, CNDO/S and INDO/S approximations taking into account singly excited electronic configurations.^{21, 29, 43, 56, 64, 65} The calculated spectra of DD and β -TCDD, in comparison with the experimental spectra, are presented in Figs 5 and 6. It can be seen that, although the absolute magnitudes of energies in the calculated spectra usually prove to be overestimated, the calculations represent satisfactorily the general pattern of the absorption spectrum, *i.e.* the relative arrangement and the relative intensities of the weak and strong bands.

According to calculations,^{29, 43, 65} the spectral region corresponding to the long-wavelength band A contains the frequencies of the first four electronic transitions from S_0 to $\pi\pi^*$ states, namely, B_{3g} , B_{2u} , A_g and B_{1u} but only two of these states are dipole-active. Note that the mutual arrangement of the energy levels corresponding to the first three electronic states changes

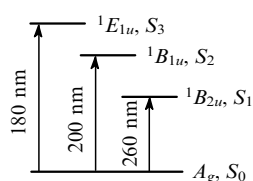
depending on the parametrisation accepted in the semiempirical calculations; thus, the S_1 state can belong to the B_{3g} , B_{2u} and A_g types. To the best of our knowledge, no experimental data on the type of symmetry of the S_1 state are available. The S_4 state in dioxins has B_{1u} symmetry.

The short-wavelength absorption bands **B** and **C** are due to the third and fourth dipole-allowed transitions from $\pi\pi^*$ states with the B_{2u} and B_{1u} types of symmetry, respectively (see Figs 5, 6).

The calculations of electronic states showed that the structure of the $\pi\pi^*$ -absorption spectrum indicated above does not change substantially in the sequence DD, β -TCDD, α,β -TCDD and OCDD; the increase in the number of chlorine atoms in the molecule changes somewhat the energies of these states (this is in agreement with the experimental results pointing to the small difference between the positions of the band maxima in the UV spectra of various dioxins). The slight influence of the increase in the number of chlorine atoms on the $\pi\pi^*$ -absorption spectrum is also known for other molecules (for example, for chlorinated 9,10-anthraquinones⁶⁶).

It should be mentioned that the calculation, which describes satisfactorily the relative oscillator strengths for transitions, reproduces poorly, as a rule, their absolute magnitudes. For example, according to experimental data ($\epsilon_A = 0.37 \times 10^4$ litre mol⁻¹ cm⁻¹), band **A** of the DD molecule corresponds to the oscillator strength $f_A = 0.067$.²⁹ Various semiempirical calculations which used different molecular models and different approximations or parametrisations gave the following f_A values for DD corresponding to the sum of the oscillator strengths of the first two dipole-active transitions: $f_A = 0.368$,²¹ 0.032²⁹ and 0.17.^{64, 65} The calculated^{64, 65} relative f_B/f_A values for the DD, β -TCDD and OCDD molecules ($f_B/f_A = 9.8, 6.2$ and 70, respectively) agree in order of magnitude with the ratios of extinction coefficients found experimentally (10, 9 and 35, respectively^{56, 58}). Thus, the calculation of the electronic states for planar models of the molecules confirms the experimental data^{56, 58} concerning the substantial decrease in the absorption cross-section at 305 nm for OCDD molecule relative to the DD or β -TCDD molecules.

The **A**–**C** bands in the singlet–singlet $\pi\pi^*$ -absorption spectrum of DD (or other dioxins) can be matched to the corresponding bands in the benzene spectrum. Scheme 1 shows three transitions from states with different types of symmetry and the corresponding absorption maxima for benzene.⁶⁷



Scheme 1

The $B_{2u} \leftarrow S_0$ and $B_{1u} \leftarrow S_0$ transitions are dipole-inactive in the D_{6h} symmetry group and are allowed only upon vibronic (Herzberg–Teller) coupling.

The B_{1u} and B_{2u} states of benzene should be matched to four states of the DD molecule with D_{2h} symmetry, which contains two benzene fragments, namely, B_{2u} and A_g (analogues of B_{2u} in benzene) and B_{1u} and B_{3g} (analogues of B_{1u} in benzene). In the D_{2h} symmetry group, the B_{2u} and B_{1u} states are dipole-active but (in line with their origin) they are characterised by low oscillator strengths. These four transitions correspond to one weak, the longest-wavelength band **A** in dioxins (see Figs 5, 6).

The band with a maximum at 180 nm in the spectrum of benzene is due to the dipole-active $E_{1u} \leftarrow S_0$ transition. In molecules with D_{2h} symmetry, for example in DD, two (according to the number of benzene fragments) electronic states E_{1u} of benzene are matched by the B_{2u} , B_{1u} , A_g and B_{3g} states. The u -type states (B_{2u} and B_{1u}) in DD and in other dioxins should be identified with intense absorption bands **B** and **C** with maxima at about ~ 250 nm. According to calculations, they are characterised by great oscillator strengths of transitions.

The analogy between the electronic states of benzene and dioxins is confirmed by calculations of the corresponding π -MO of the molecule.²⁸ Indeed, for at least six lower electronic states, the symmetry of the π -MO of benzene is approximately retained in the benzene fragments of DD. This is reflected, for example, in Fig. 1, which shows the distribution of the coefficients at the $2p_x$ -AO centred on the atoms of the six-membered benzene fragments of the molecule for four MO. It can be seen that this distribution is similar to the known distribution of the coefficients in the vacant (E_{1g}) and occupied (E_{2u}) π -MO of benzene.

The oxygen atoms have little influence on the local symmetry of the MO under study, although the lone electron pairs (l -electrons) of oxygen, which occupy the $2p_x$ -AO, also contribute to π -conjugation (when this is allowed by the type of symmetry of the whole MO of the molecule). They bring about the greatest perturbation of occupied rather than of vacant MO of dioxins.^{28, 56} For the highest occupied MO of the DD molecule, this contribution is 26%; in the S_1 state, 0.15 of an electron charge is transferred from the oxygen atoms to the carbon atoms of the benzene fragments.

The effect of l -electrons on the S_1 state normally shows itself as a substantial decrease in the energy of the π/π^* state with respect to the $\pi\pi^*$ state and as an increase in the corresponding dipole moment of the transition. For dioxins, this influence of the l -electrons of oxygen and chlorine on the S_1 state is slight; hence, the π/π^* state can be designated by $\pi\pi^*$.

In dioxins, the lone electron pairs (n electrons), which occupy $2p_z$ - or $2p_y$ -AO, form very deeply located MO and the absorption bands corresponding to the $n\pi^* \leftarrow S_0$ transitions should occur in the vacuum UV region. According to calculations,⁶⁵ the spectral region between absorption bands **A** and **B** of dioxins, as in the case of benzene, contains bands corresponding to the $\pi\sigma^* \leftarrow S_0$ transitions.

The analogy between the electronic transitions in DD and benzene (with allowance for the slight influence of chlorine atoms on the spectrum) accounts for the distribution of band intensity in the UV spectra of dioxins.

The same analogy can be drawn between the $\pi\pi^*$ electronic states of benzene, DD and other molecules, for example, 9,10-anthraquinone and anthracene, which contain, like DD, two benzene side fragments. The DD, 9,10-anthraquinone and anthracene molecule differ in the central fragments. Comparison of the spectral and theoretical data concerning their $\pi\pi^*$ states demonstrates the influence of the electronic structure of the central fragment on the mutual arrangement of the first four energy levels. Recall that the first four electronic transitions in DD are responsible for one band **A**. According to theoretical and experimental data,⁶⁸ in 9,10-anthraquinone, the energy level of the state analogous to the $S_4(B_{1u})$ state of DD proves to be shifted to short-wavelength region with respect to the first states B_{2u} , B_{3g} and A_g to such an extent that a separate band with a maximum at ~ 270 nm is attributed to the corresponding transition. Conversely, in the anthracene molecule, the energy level of the state analogous to $S_4(B_{1u})$ in DD is shifted to longer wavelengths with respect to the other three states; thus, it becomes the $S_1(B_{1u})$ state and the onset of the band corresponds to a wavelength of ~ 280 nm.^{53, 69}

Let us briefly summarise the data on the singlet–singlet transitions in dioxins. The long-wavelength band in the absorption spectrum has a combination structure in the sense that it ‘hides’ transitions from the four electronic states having different types of symmetry: B_{1u} , B_{3g} , A_g and B_{2u} , where B_{1u} corresponds to the S_4 state. Variation of the number of chlorine atoms from zero (DD) to eight (OCDD) does not change generally this structure of the band but results in a nearly parallel shift of the energy levels of the corresponding states towards lower frequencies. The mutual arrangement of the energy levels of the B_{1u} and B_{2u} states changes substantially only in a series of molecules having similar structures but containing different atomic groups in the central fragment, for example, in the series of DD, 9,10-anthraquinone and anthracene, in which the above-mentioned states are of the same nature. Thus,

the structure of the long-wavelength band in the spectra of dioxins is determined by the presence of the ether C—O—C groups in the central fragment.

The energy levels calculated for the B_{2u} , B_{3g} and A_g states in dioxins are close; therefore, additional investigations are required to determine the type of symmetry of the S_1 state of a particular molecule. For example, it would be useful to obtain and study the fine vibrational structure of the fluorescence spectrum.

The low intensity of the long-wavelength band in the spectra of dioxins is due to its origin: the electronic transitions corresponding to this band are analogues of the first two, dipole-inactive transitions in benzene. The change in the number of chlorine atoms generally has little influence on the intensity distribution in the UV spectra of dioxins.

V. Luminescence

Dioxins belong to the class of luminescing compounds. Luminescence is due to the $S_1 \rightarrow S_0$ transition from the lower singlet electronically excited state (fluorescence) and to the $T_1 \rightarrow S_0$ transition from the lower triplet state (phosphorescence). Solutions of dioxins fluoresce in the region of 310–400 nm; when frozen (77 K), they display a bright long-living blue to light-blue phosphorescence. As an example, Fig. 8 presents the emission spectrum of a solution of DD in isopentane recorded at 77 K.⁵⁶ This spectrum demonstrates an important feature characteristic of both DD and PCDD, namely, very low intensity of the fluorescence band 1 with respect to the phosphorescence band 2.

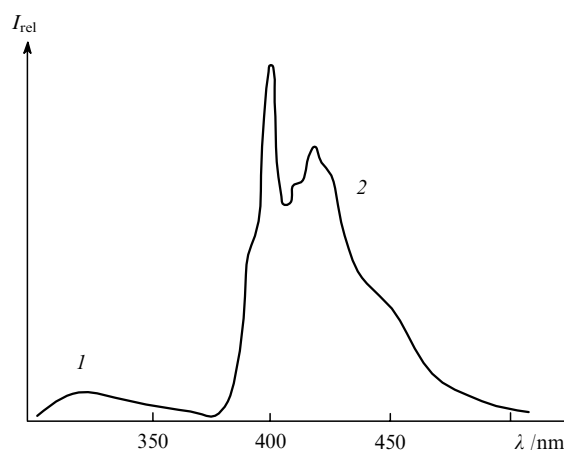


Figure 8. Luminescence spectra of a solution of DD in isopentane at 77 K;⁵⁶ (1) fluorescence, (2) phosphorescence.

1. Photophysical characteristics of luminescence

In this Section, the quantitative data on the deactivation of the first singlet and triplet electronically excited states of dioxins are presented. We discuss experimental values for the quantum yields and the decay times of fluorescence (ϕ_f and τ_f) and phosphorescence (ϕ_{ph} and τ_{ph}), the rate constants for deactivation of the lower singlet and triplet electronically excited states (k_f and k_{ph}), theoretical estimates of the k_{ph} values, and the results of calculations of the influence of the number of chlorine atoms in the molecule on k_{ph} and τ_{ph} .

a. Fluorescence

The fluorescence spectra of solutions of DD and PCDD exhibit a structureless band (see Fig. 8). The use of selective laser excitation of fluorescence, which often gives rise to a fine (vibrational) structure in the spectra of solutions,⁷⁰ still has not allowed recording of structured spectra for the molecules under study (β -TCDD, 1,3,7,8-Cl₄DD and OCDD).⁵⁸

The most complete experimental data, reported in the literature, on the deactivation of the S_1 state for solutions of DD in isopentane^{29, 56} and ethanol⁷¹ are presented below.

ϕ_f	τ_f / ns	k_f / s ⁻¹	Ref.
0.003	3.5	0.9×10^6	56
0.000	< 1	—	71
—	—	1.6×10^7	29

For β -TCDD, an approximate estimate gave $\tau_f \approx 10$ ns (vapour, 473 K)⁵⁸ and $k_f \approx 4.0 \times 10^7$ s⁻¹ (vapour and a solution in CHCl₃, 77 K).²⁹ The difference between the given ϕ_f and τ_f values determined for DD in the publications cited is due to the fact that the measurements were performed near the limit of the capacity of the equipment employed and to the influence of the solvent.

The k_f values for isopentane solutions of DD have been determined by different methods.^{29, 56} For DD (as well as for β -TCDD), the k_f values for the $S_1(B_{2u}) \rightarrow S_0$ transition were estimated²⁹ using the calculated data on the ratio of the oscillator strengths of the $^1B_{2u} \leftarrow S_0$ and $^1B_{1u} \leftarrow S_0$ transitions, which are responsible for the long-wavelength band A in the absorption spectra, and experimental data on the integrated intensity of this band (see Figs 5, 6). The k_f values found in this way are over-estimated because the integrated extinction coefficient of band A can contain contributions of the transitions caused by the Herzberg–Teller vibronic coupling. In another method,⁵⁶ the k_f value was estimated from the expression $k_f = \phi_f / \tau_f$.

It is difficult to explain this great (by an order of magnitude) discrepancy of the k_f values found for DD. The main reason may be as follows. One value²⁹ corresponds to the dipole-allowed $^1B_{2u} \rightarrow S_0$ transition. The other, smaller k_f value⁵⁶ might refer to the emission from a g -type rather than u -type S_1 singlet state, for example, to the $^1A_g \rightarrow S_0$ transition, *i.e.* to a transition allowed only with account of the Herzberg–Teller intramolecular interactions. Some possible errors both in spectral measurements and in quantum-chemical calculations should also be taken into account.

An interesting dependence of the fluorescence and phosphorescence quantum yields on the structural factor for the series DD, dihydroanthracene and xanthene has been found.⁵⁶

	Dihydroanthracene	Xanthene	DD
ϕ_f	0.26	0.26	0.003
ϕ_{ph}	0.14	0.14	0.4

Despite the fact that the dihydroanthracene and xanthene molecules have the same luminescence quantum yields, the ϕ_f value for DD is much smaller. Meanwhile, the ϕ_{ph} value for DD is almost 3 times as great as those for dihydroanthracene or xanthene.

According to calculations,⁵⁶ the S_1 state in the xanthene and DD molecules can be assigned to the π/π^* type of orbital; the change in the π -electron density on the oxygen atoms in this state is nearly the same for these two molecules. Therefore, the sharp (by two orders of magnitude) decrease in the ϕ_f value for DD with respect to xanthene is believed to be due to the higher rate constant for the $S_1 \rightarrow T_j$ intersystem crossing (k_{isc}) in the case of DD.

It is known that the k_{isc} values for the transfer of energy between states of different orbital natures, $\pi\pi^*$ and $n\pi^*$ (or $\sigma\pi^*$), are several orders of magnitude higher than those for states with the same orbital nature ($\pi\pi^*$ and $\pi\pi^*$).⁷² For this reason, the higher k_{isc} value found for DD was interpreted⁵⁶ by assuming that only DD possesses a T_j state of the $n\pi^*$ type the energy of which is very close to the energy of S_1 . This arrangement is believed to be due to the lowering of the energy levels of the $n\pi^*$ states in this molecule (containing two oxygen atoms) with respect to those in the xanthene molecule (with one oxygen atom). However, it follows from the calculations for the $n\pi^*$, $\pi\sigma^*$ and $\sigma\pi^*$ states that the energies of the corresponding triplet levels of the DD

molecule are more than $10\,000\text{ cm}^{-1}$ higher than the energy of the S_1 state.^{29,65} These states cannot ensure high k_{isc} . The difference between the ϕ_{n} values in xanthene and DD might be due to the difference between the symmetries of the xanthene (C_{2v}) and DD (D_{2h}) molecules, in particular, to the fact that the S_1 state in the DD molecule might correspond to the g type: the first line in the spectrum of the $S_1 \leftarrow S_0$ transition shown in Fig. 7 has a relatively low intensity. In our opinion, the question of what is the reason for the low ϕ_{n} value in DD remains open.

b. Phosphorescence

Phosphorescence is manifested as a relatively intense band in the spectrum shown in Fig. 8. Using specific experimental conditions, spectra with clear-cut vibrational structure of this band have been obtained for DD and PCDD (see Section V.2).

For a number of dioxins, the phosphorescence lifetimes τ_{ph} at 77 K have been measured.^{2,43,56,64,65,73} For example, in the case of DD, $\tau_{\text{ph}} = 0.54\text{ s}$ (77 K, a solution in a 1:5:5 mixture of ethanol, isopentane and ether)² and 0.7 s (77 K, a solution in isopentane).⁵⁶ For chloro-substituted derivatives, the phosphorescence lifetimes are shorter than for unsubstituted DD.²

In the case of PCDD, the τ_{ph} values found by different researchers can be substantially different. Thus for a number of dioxins (ranging from mono- to octa-substituted derivatives), τ_{ph} values varying from 0.29 to 0.075 s have been reported.² According to another publication,⁷³ the τ_{ph} values for another series of tetra- and penta-substituted dioxins in *n*-hexane vary over the 1.55–1.03 s range. The τ_{ph} values presented in the two publications^{2,73} for the only compound common to both of them, 1,2,3,4-Cl₄DD, differ by more than an order of magnitude — 0.057 and 1.03 s. Both groups of researchers noted little differences in the τ_{ph} values within the series of dioxins they studied. Shorter τ_{ph} values were found² for those dioxins which contain several (3 or 4) Cl atoms in only one benzene fragment.

The great discrepancies between τ_{ph} found for PCDD in different studies are apparently due to some systematic error of measurements (rather than to the use of different solvents). For OCDD, β -TCDD and α,β -TCDD as solutions in *n*-hexane, the times τ_{ph} have been measured (see below) at 77 K.^{43,64,65} These values were found to be in satisfactory agreement with τ_{ph} measured for solutions in a 1:5:5 mixture of ethanol, isopentane and ether.²

	OCDD	β -TCDD	α,β -TCDD
<i>n</i> -Hexane			
$\tau_{\text{ph}}/\text{s}$	0.30	0.20	0.30
Solvent mixture			
$\tau_{\text{ph}}/\text{s}$	0.25	—	0.25

The radiative $T \rightarrow S_0$ transitions are allowed due to intramolecular spin-orbit (SO) and vibronic-spin-orbit (VSO) couplings.^{74,75} Correspondingly, the rate constant k_{rad} for the radiative deactivation of the triplet state can be represented as $k_{\text{rad}} = k_{\text{SO}} + k_{\text{VSO}}$; in the case of phosphorescence, $T = T_1$ and $k_{\text{rad}} = k_{\text{ph}}$. It has been proposed to use the data on the distribution of the intensity in fine-structure electronic-vibrational phosphorescence spectra for estimating the k_{VSO} to k_{SO} ratio.⁷⁶ These estimates obtained for the T_1 states of DD, β -TCDD and OCDD show⁴² that the magnitudes of the phosphorescence rate constants k_{ph} for these molecules are stipulated by different mechanisms of intramolecular interactions. More precisely, this constant for DD is determined by only vibronic-spin-orbit coupling, while in β -TCDD and OCDD, they are determined by both spin-orbit and vibronic-spin-orbit couplings (see Section V.2).

Let us dwell now on the data on k_{ph} . It follows from the τ_{ph} and ϕ_{ph} values measured for the DD molecule⁵⁶ that $k_{\text{ph}} = 0.57\text{ s}^{-1}$, $k_{\text{SO}} = 0$; hence, $k_{\text{ph}} = k_{\text{VSO}}$. For PCDD, no experimental data on k_{ph} are currently available, although the τ_{ph} values are known; they can be found from the relation

$$\tau_{\text{ph}} = \frac{1}{k_{\text{ph}} + k_{\text{nr}}^T},$$

where k_{ph} is the rate constant for the radiative and k_{nr}^T is the rate constant for the non-radiative deactivation of the T_1 state. For several dioxin molecules, the k_{SO} , k_{VSO} and k_{ph} values have been estimated theoretically.^{43,64,65}

Quantum-chemical calculations were employed to estimate the k_{SO} values for DD, β -TCDD, α,β -TCDD and OCDD; it was found^{43,64,65} that the number and the arrangement of Cl atoms in the molecule influences k_{SO} values for the $^3B_{1u}$ states. First, it was concluded that each heteroatom (O, α -Cl or β -Cl) in these molecules makes an additive contribution to the dipole moment of the P_{0-0} transition (the square of which is related to k_{SO}). Second, a cancellation effect of the α -Cl and β -Cl atoms on the P_{0-0} value was found. As a result, it was found that $k_{\text{SO}}(\beta\text{-TCDD})/k_{\text{SO}}(\text{OCDD}) = 3.6$, *i.e.* the decrease in the number of Cl atoms in the molecules of β -TCDD with respect to that in OCDD (by a factor of two) induces a substantial increase rather than a decrease in the k_{SO} component of the k_{rad} rate constant. It was concluded^{43,65} that the cancellation effect of several heteroatoms (chemically identical but differing in the position in the molecule) on the spin-orbit coupling, found in the study of dioxins, could be useful in elucidating the reasons for the known abnormal influence^{77,78} of an internal heavy atom on the k_{ph} and τ_{ph} values in some organic molecules.

The use of calculated k_{SO} values and experimental data on the $k_{\text{SO}}/k_{\text{VSO}}$ ratio gave the following estimates for the rate constants k_{ph} for β -TCDD and OCDD: 7 and 5 s^{-1} . Modelling of the k_{nr}^T values made it possible to determine theoretically⁶⁴ the ratio of τ_{ph} for these molecules [$\tau_{\text{ph}}(\text{OCDD})/\tau_{\text{ph}}(\beta\text{-TCDD}) = 1.6 \pm 0.2$], which is consistent with the experimental value 1.5 (the experimental data on τ_{ph} were mentioned above). The theoretical absolute magnitudes of τ_{ph} for these molecules also proved to be close to experimental values. For instance, for OCDD, the calculated value was $\tau_{\text{ph}} = 0.10\text{--}0.20\text{ s}$.

2. Fine-structure phosphorescence spectra

In this Section, we consider the results of investigations of fine-structure phosphorescence spectra of dioxins concerning the energies and types of symmetry of lower triplet electronic states, the frequencies and types of symmetry of vibrations (in particular, low-frequency vibrations), and the contributions of intramolecular spin-orbit and vibronic-spin-orbit couplings to the phosphorescence rate constant. The results of theoretical calculations for the change in the electron density and the estimates of the change in the molecular geometry in the lower excited triplet $\pi\pi^*$ state with respect to the ground electronic state are presented.

a. Spectra at 77 K

Below we consider experimental data on the influence of solvents (non-branched alkanes) on the pattern of the low-temperature phosphorescence spectra of dioxins.

The fine structure of broad-band phosphorescence spectra (see, for example, Fig. 8) can be recorded under specific conditions, which include conducting the experiment at low temperatures, selection of the appropriate solvent and, in some cases, selection of a particular wavelength of the exciting light.^{70,79} These experimental conditions should ensure low electron–phonon interactions and slight inhomogeneous or homogeneous spectral broadening.^{70,80} A well-known method for recording the structured luminescence spectra of complex organic compounds is the Shpol'skii method,⁷⁹ based on the use of *n*-alkanes (*n*-hexane, *n*-heptane, *n*-octane, *etc.*), which form a polycrystalline material at low temperatures, as solvents. These solvents ensure slight inhomogeneous broadening of the spectrum. Upon deep cooling of solutions of luminescent molecules in these solvents down to the boiling point of liquid nitrogen (77 K) or liquid helium (4.2 K), the electron–phonon interaction and homogeneous broadening of the spectrum decrease.⁸⁰ As a con-

sequence, the electronic-vibrational (vibronic) emission spectra consist of a large number of quasi-lines (lines). These spectra are referred to as quasi-line or fine-structure spectra.

The vibrational structure of the phosphorescence spectra of DD and PCDD was revealed at 77 K for solutions in a 1:5:5 mixture of ethanol, isopentane and ether² and in normal hydrocarbons.^{81,82} When the Shpol'skii method is used to make the structure of the spectrum as clear as possible at a specified temperature, it is important to select an appropriate solvent. The Bolotnikova rule⁸³ concerning the commensurability of the linear dimensions of the molecules of the solvent and of the compound under study serves as a criterion for choosing the solvent. Since dioxins are highly toxic, the problem of selecting the solvent has been studied in detail only for DD.⁸¹ It was established that the most clear spectrum is observed in n-hexane and n-heptane matrices (Fig. 9). The spectral patterns in these solvents are more structured than in a 1:5:5 mixture of ethanol, isopentane and ether.

The structured phosphorescence spectra of solid solutions exhibit so-called components of the Shpol'skii multiplet, which are due to luminescence of different centres. Each of the luminescence centres is matched by lines for transition to vibrational sublevels of the ground electronic state (this is the vibronic structure of the spectrum) and by a line corresponding to a purely electronic transition (if it is dipole-allowed) with the frequency ν_{0-0} . As a consequence, the spectrum often has a very intricate structure. At 77 K, the lines are normally markedly broadened due to the phonon wing and they are often called quasi-lines.^{62,70}

Table 6 lists the quasi-line maxima (1–9) in the spectra of DD and PCDD;⁸² only for 1,2,3,4,6-Cl₅DD was it impossible to obtain a quasi-line spectrum in solid solutions in hydrocarbons. The spectrum of this compound was a broad structureless band with a maximum at 480 nm. The same spectral pattern with a maximum at 485 nm was obtained for solutions of 1,2,3,4-Cl₄DD in a 1:5:5 mixture of ethanol, isopentane and ether and in n-hexane at 77 K.^{2,73}

Now we consider briefly the possible reason for the absence of structure and the bathochromic shift of the phosphorescence band in the spectra of solutions of 1,2,3,4-Cl₄DD^{2,73} and 1,2,3,4,6-Cl₅DD.⁸² A specific feature of these molecules is that one benzene ring in them is fully chlorinated, while the other contains either no chlorine atoms or only one atom. Molecules with so asymmetric an arrangement of chlorine atoms are polar.

It has been shown that polar molecules of oxygen-containing compounds dimerise in solutions in saturated hydrocarbons.⁸⁴ Thus the broad structureless bands in the phosphorescence spectra of 1,2,3,4-Cl₄DD and 1,2,3,4,6-Cl₅DD may belong to their dimers. However, to elucidate more definitely the reason for the structure-

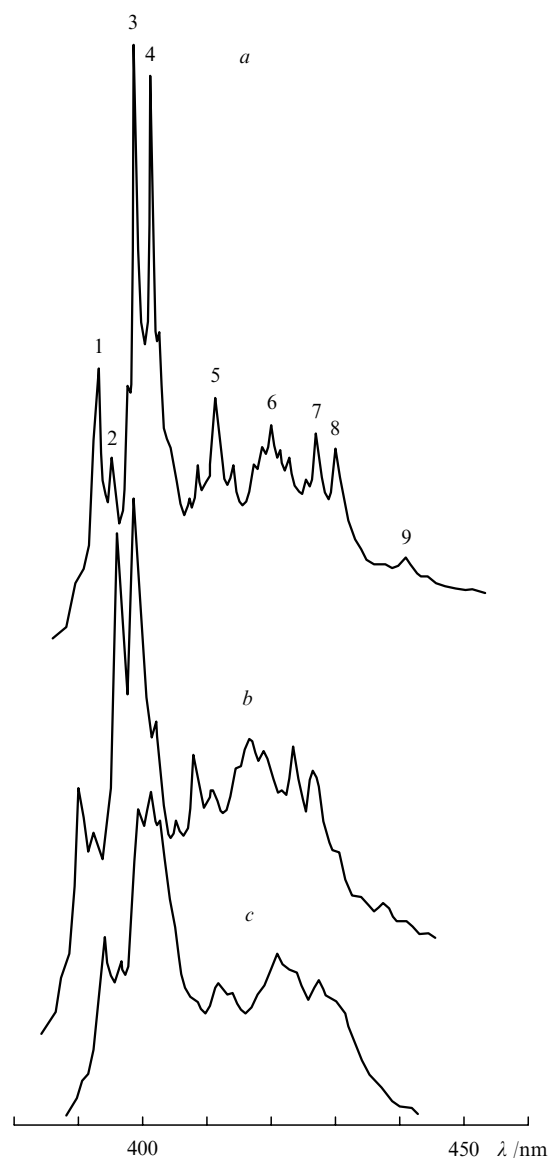


Figure 9. Phosphorescence spectrum of solutions of DD in n-hexane (a), n-heptane (b) and n-octane (c) at 77 K.⁸¹ The λ values in the maxima of the numbered lines are given in Table 6.

Table 6. Positions of the quasi-line maxima in the phosphorescence spectra of solutions of dioxins in n-hexane at 77 K.⁸²

Compound	λ / nm								
	1	2	3	4	5	6	7	8	9
DD	394	396	400	402	412	420	427	430	441
2-ClDD	396	399	402	408	410	414	424	430	
2,3-Cl ₂ DD	402	406	407	412	416	429			
2,3,8-Cl ₃ DD	403	407	408	410	415	418	432		
2,3,7,9-Cl ₄ DD	406	410	412	417	420	428	434	438	
2,3,8,9-Cl ₄ DD	406	407	410	417	428	434	439		
β -TCDD	410	412	417	421	433	438	441	447	
α,β -TCDD	409	411	415	417	419	426	433	437	440
1,2,3,7,8-Cl ₅ DD	410	413	415	421	436	442	451		
1,2,3,4,6-Cl ₅ DD	480								
1,2,3,4,7,8-Cl ₆ DD	408	415	420	426					
1,2,3,6,7,8-Cl ₆ DD	414	417	424	440	443	446			
OCDD	419	423	430	436	443	449	454	462	

Note. The numerals 1 to 9 mark the numbers of lines in the spectra. The wavelengths corresponding to the most intense quasi-lines in the phosphorescence spectra are typed in bold.

less spectral pattern and the bathochromic shift of the phosphorescence band in the spectra of these compounds with respect to the spectra of other PCDD, additional investigations are needed.

Data on the positions of the quasi-line maxima in the spectra and on the distribution of the relative intensities of quasi-lines led to the conclusion^{82, 85} that these spectra are highly individual and could be used for identification of various dioxins, in particular, isomers (see Section VI).

b. Spectra at 4.2 K

Study of the phosphorescence spectra of a number of dioxins at 4.2 K (see compounds in Table 6) showed⁸² that, as the temperature decreases from 77 to 4.2 K, the half-width of the quasi-lines decreases by an order of magnitude (to 0.2–0.5 nm), while the peak intensity of lines increases. In addition, whereas the spectra recorded at the boiling point of liquid nitrogen consist, on the average, of 10–15 quasi-lines, the spectra at 4.7 K contain several dozens of quasi-lines.

At low temperatures (for example, 4.2 K), the vibronic structure of the emission spectra is due to the transitions from the zero vibrational sublevel of the electronically excited state to various vibrational sublevels of the ground electronic state S_0 . This spectrum contains vibration frequencies which are detected in the vibrational spectra (IR and Raman). As an example, Figure 10 shows a fine-structure phosphorescence spectrum of a solution of DD, while Table 7 presents the assignment of the structure of this spectrum,⁴¹ namely, determination of the components of the Shpol'skii multiplet, the frequencies of purely electronic transitions ν_{0-0} , the frequencies of the fundamental vibrations and the sum vibration frequencies. A similar analysis of the spectral structure has been carried out for solutions of β -TCDD, α,β -TCDD and OCDD.^{39, 42, 43}

The $T_1 \rightarrow S_0$ transition, which is spin forbidden, becomes allowed as a result of spin-orbit and vibronic-spin-orbit couplings.^{74, 75} As a consequence, the fine-structure electronic spectra do not exhibit all vibrations but only totally symmetric vibrations and some types of non-totally symmetric ones. By taking account of the characteristic matrix elements⁷² for the spin-orbit coupling and of the dipole moments of the ${}^1\sigma\pi^* \rightarrow S_0$ and ${}^1\pi\pi^* \rightarrow S_0$ transitions, which influence the line intensity, it can be concluded³⁰ that the out-of-plane vibrations may be responsible for intense lines in the $\pi\pi^*$ phosphorescence spectra. Vibronic lines of

this type are actually observed in the phosphorescence spectra of dioxins (see Figs 10, 11 and Table 7).

Determination of the symmetry of the T_1 state in dioxins is difficult. According to quantum-chemical calculations,^{29, 65} the two $\pi\pi^*$ triplet states lowest in energy (more precisely, π/π^*) correspond to electronic functions of g and u types, the T state of the u type being analogous in orbital structure to the fourth $\pi\pi^*$ singlet state $S_4(B_{1u})$, the band of which is 'hidden' in the long-wavelength absorption band (see Figs 5, 6). The difference between the energies of the two T states is small ($\sim 1000 \text{ cm}^{-1}$); hence, variation of the positions of chlorine atoms in PCDD molecules can change the mutual arrangement of these triplet states. However, the accuracy of calculations does not suffice for deciding which of the states with the calculated types of symmetry B_{3g} and B_{1u} is the lowest (T_1). Moreover, the $\pi\pi^*$ phosphorescence spectra of dioxins the molecules of which have an inversion centre can exhibit intense lines corresponding to out-of-plane vibrations for both symmetry forbidden (when T_1 belongs to the g type of symmetry) and symmetry allowed (when T_1 belongs to the u type of symmetry) transitions.

The question of the type of symmetry of the T_1 state can be answered by determining the type of symmetry of non-totally symmetric vibrations the frequencies of which $\nu(\text{phos})$ are observed in the phosphorescence spectra. For the $T_1 \rightarrow S_0$ transitions from the states corresponding to g or u symmetry, non-totally symmetric (out-of-plane) vibrations of only a particular type of symmetry, either u or g , respectively, can manifest themselves, in conformity with the selection rules.⁷⁵ This regularity was used^{39, 41–43} to determine the type of symmetry of the T_1 state of dioxins. These states in DD, β -TCDD and OCDD were assigned to different (B_{3g} and B_{1u}) types of symmetry (Fig. 12). The experimental values of the energies (ν_{0-0}) of the T_1 state and the corresponding k_{SO}/k_{VSO} ratios for the components of the phosphorescence rate constants have also been determined for these compounds.⁴²

	DD	β -TCDD	OCDD
$\nu_{0-0} / \text{cm}^{-1}$	25595	24410	23836
$k_{SO} : k_{VSO}$	0 : 1	1 : 0.7	1 : 3.3

The ν_{0-0} frequencies of purely electronic transitions, $T_1 \rightarrow S_0$, either allowed or forbidden from the orbital symmetry standpoint,

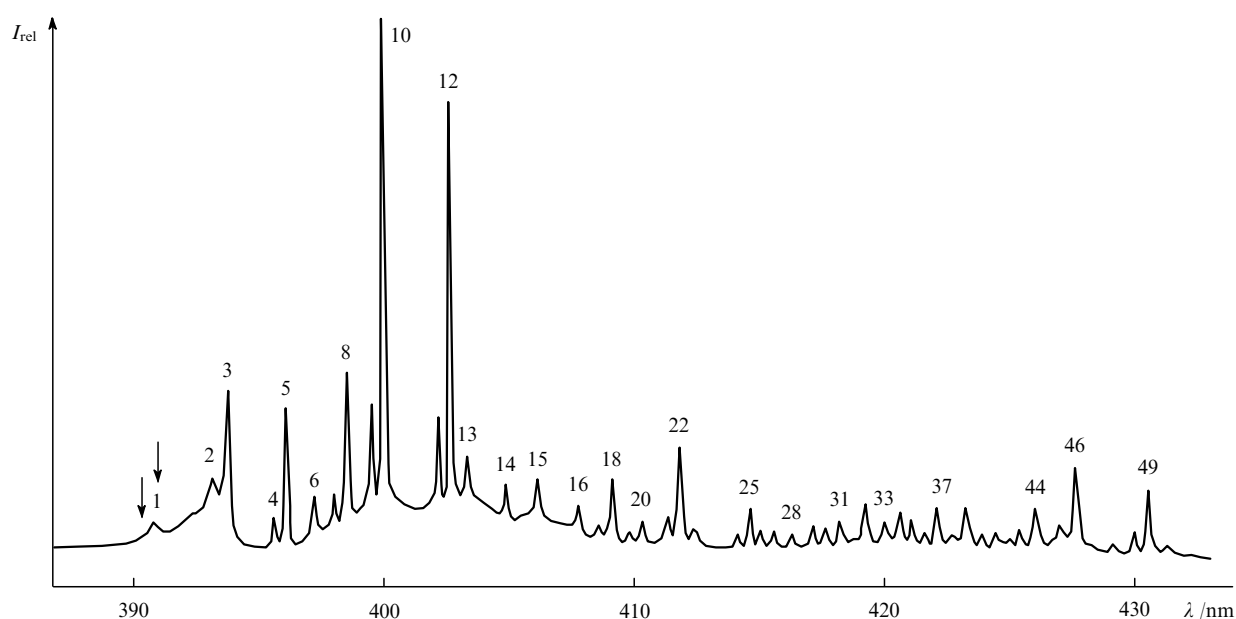


Figure 10. Phosphorescence spectrum of DD in n-hexane at 4.2 K.⁴¹ The interpretation of the spectrum is given in Table 7. The arrows mark the positions of the Shpol'skii multiplet components corresponding to a purely electronic transition.

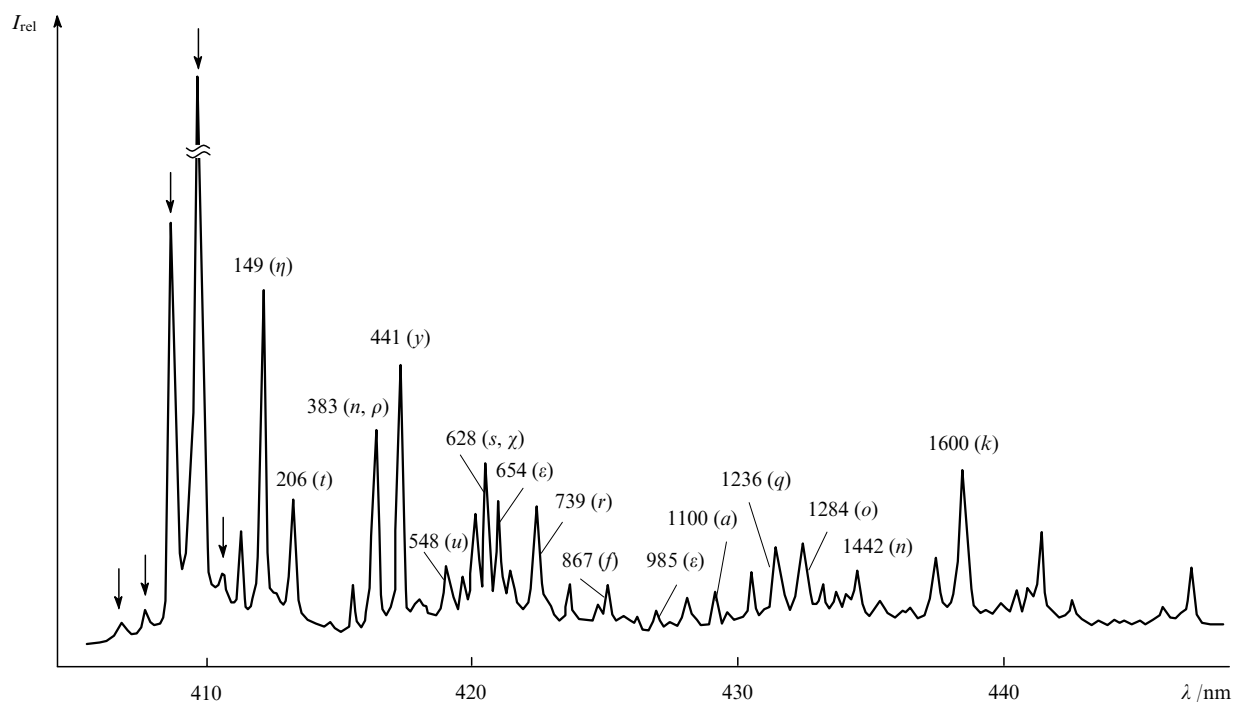


Figure 11. Phosphorescence spectra of β -TCDD in n-hexane at 4.2 K.³⁹ The arrows mark the positions of the Shpol'skii multiplet components corresponding to a purely electronic transition. In the line maxima of the most intense multiplet components, the frequencies (cm^{-1}) of only fundamental modes are given. The assignment of vibrations is given in parentheses (see Table 1).

Table 7. Positions of the line maxima (ν_N/cm^{-1}) and interpretation of the phosphorescence spectra of DD in n-hexane (see Fig. 10).

Line number <i>N</i>	ν_N/cm^{-1}	Components of the Shpol'skii multiplet	$\Delta\nu^a$	Interpretation ^b	Line number <i>N</i>	ν_N/cm^{-1}	Components of the Shpol'skii multiplet	$\Delta\nu^a$	Interpretation ^b
	25628	I	0	0-0	25	24134	II	1461	$\nu_5 + \nu_{10}$ (722)
1	25595	II	0	0-0	26	24116	II	1479	?
2	25439	I	189	ν_1 (<i>h</i>)	27	24081	II	1514	?
3	25407	II	188	ν_1 (<i>h</i>)	28	24035	II	1560	?
4	25296	I	332	ν_2 (<i>y</i>)	29	23992	II	1603	$\nu_4 + \nu_{11}$ (1027)
5	25266	II	329	ν_2 (<i>y</i>)	30	23964	II	1631	$\nu_3 + \nu_{12}$ (1146)
6	25188	III		0-0 ?	31	23931	II	1664	?
7	25141	I	487	ν_3 (<i>z</i>)	32	23873	II	1722	$\nu_4 + \nu_{12}$ (1146)
8	25110	II	485	ν_3 (<i>z</i>)	33	23830	II	1765	$\nu_5 + \nu_{11}$ (1026)
9	25052	I	576	ν_4 (<i>o</i>)	34	23792	II	1803	$\nu_4 + \nu_{13}$ (1227)
10	25019	II	576	ν_4 (<i>o</i>)	35	23766	II	1829	?
11	24887	I	741	ν_5 (<i>g</i>)	36	23738	I	1890	$\nu_5 + \nu_{12}$ (1149)
12	24856	II	739	ν_5 (<i>g</i>)			II	1857	$\nu_4 + \nu_9 + \nu_{10}$ (715)
13	24814	II	781	ν_6 (<i>v</i>)	37	23710	II	1885	$\nu_5 + \nu_{12}$ (1146)
14	24719	II	876	ν_7 (<i>i</i>)	38	23672	I	1956	$\nu_5 + \nu_{13}$ (1215)
15	24639	II	956	ν_8 (<i>j</i>)	39	23646	II	1949	$\nu_5 + \nu_{13}$ (1210)
16	24535	II	1060	$\nu_3 + \nu_9$ (575)					$\nu_2 + \nu_{14}$ (1620)
17	24484	I	1144	$\nu_4 + \nu_9$ (568)	40	23610	II	1985	?
18	24453	II	1142	$\nu_4 + \nu_9$ (566)	41	23571	II	2024	$\nu_5 + \nu_9 + \nu_{10}$ (719)
19	24418	II	1177	?	42	23544	II	2051	?
20	24383	II	1212	$\nu_3 + \nu_{10}$ (727)	43	23520	I	2108	$\nu_3 + \nu_{14}$ (1621)
21	24325	I	1303	$\nu_4 + \nu_{10}$ (727)	44	23491	II	2104	$\nu_3 + \nu_{14}$ (1619)
				$\nu_5 + \nu_9$ (562)	45	23428	I	2200	$\nu_4 + \nu_{14}$ (1624)
22	24295	II	1300	$\nu_4 + \nu_{10}$ (724)	46	23396	II	2199	$\nu_4 + \nu_{14}$ (1623)
				$\nu_5 + \nu_9$ (561)	47	23312	II	2283	?
23	24264	II	1331	?	48	23269	I	2359	$\nu_5 + \nu_{14}$ (1618)
24	24164	I	1464	$\nu_5 + \nu_{10}$ (723)	49	23240	II	2355	$\nu_5 + \nu_{14}$ (1616)

^a $\Delta\nu = \nu_{0-0} - \nu_N$, where ν_{0-0} is the frequency of the purely electronic transition. ^b The ordinal number *L* of the fundamental mode found in the phosphorescence spectrum is given. The frequencies ν_L , separated from the sum frequencies, with the numbers *L* = 9–14 correspond to totally symmetric fundamental vibrations (their frequencies are given in parentheses); the frequencies ν_L with the numbers *L* = 1–8 were assigned to out-of-plane vibrations of the B_{3u} and A_u types of symmetry (their letter designations are given in parentheses).

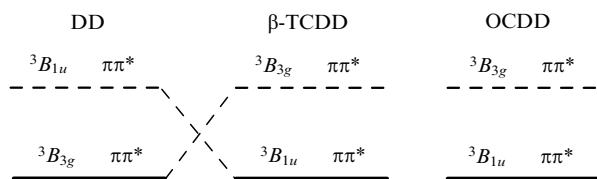


Figure 12. Symmetry of the T_1 and T_2 electronic states.⁴²

decrease somewhat in the sequence DD, β -TCDD and OCDD^{39,41–43} (the values presented above are the ν_{0-0} frequencies of one or several components of the Shpol'skii multiplet, which accounts for the most intense vibronic lines in the spectrum).

The out-of-plane vibrations of dioxins are characterised by low frequencies which are unknown from IR or Raman spectra for the vast majority of dioxins. Therefore, in the absence of experimental data, the symmetry types of the vibrations the frequencies of which $\nu(\text{phos})$ can be seen in the phosphorescence spectra can be determined by comparing the calculated vibration frequencies with $\nu(\text{phos})$. Generally, this comparison provides a satisfactory result (see the phosphorescence spectrum of β -TCDD shown in Fig. 11 and the data on the frequencies of the fundamental modes in β -TCDD listed in Tables 2–5).

The most complicated problem is to interpret the phosphorescence spectra corresponding to a forbidden purely electronic transition because in this spectrum, it is difficult to find lines due to the components of the Shpol'skii multiplet and ν_{0-0} (see, for example, Fig. 10 and Table 7, data for DD). The positions of lines corresponding to the ν_{0-0} frequencies are determined from the $\nu(\text{phos})$ values for non-totally symmetric vibrations. Therefore, to interpret these spectra, reliable experimental (from IR or Raman spectra) or theoretical data on the low-frequency vibrations of the molecule are needed.

According to the results of quantum-chemical calculations,^{43,65} the $T_2(B_{1u})$ state of the DD molecule and the $T_1(B_{1u})$ state of the β -TCDD, α,β -TCDD and OCDD molecules are very close in orbital structure and are charge transfer states. For β -TCDD, the changes in the π -electron density on atoms and on valence bonds in the T_1 state with respect to those in the S_0 state (Fig. 13) have been calculated.⁸⁶ It was concluded that in this state, charge transfer takes place from all heteroatoms of the molecule to the carbon atoms; the electron density on the C–O bonds in the central fragment of the molecule increases, which implies that the bonds are shortened.

The data on the ν_{0-0} frequencies corresponding to the singlet S_1 state²³ and the triplet T_1 state (see Fig. 12) of DD and β -TCDD molecules in solutions can be used to estimate the difference between the energies of these states — 7430 and 6940 cm^{-1} . These values are typical of aromatic molecules with an electron-

donating group;⁶⁹ this is consistent with the theoretical data on the pattern of electron density redistribution in the S_1 and T_1 states.

The distribution of the intensity of vibronic lines in the fine-structure phosphorescence spectra depends on the intramolecular interactions.^{62,63,87} The relative intensities of the vibronic lines with maxima at $\nu_{0-0} - \nu_N$ corresponding to the fundamental modes with the frequencies ν_N were measured in the phosphorescence spectra of DD, β -TCDD, α,β -TCDD and OCDD.^{39,41–43}

The intensity distribution of the lines corresponding to totally symmetric vibrations is determined by the Franck–Condon interaction, which results in a changed equilibrium geometry of the molecule in the electronically excited state. The symmetry of the nuclear configuration typical of the S_0 state is retained. The change in the geometry induces a shift of the minimum of the electron potential (Δ_{el}) along the normal vibration coordinates Q .⁶²

The Δ_{el} values were determined experimentally for the $T_1(^3B_{3g})$ electronic state of DD²⁸ and for the $T_1(^3B_{1u})$ electronic state of β -TCDD.⁸⁶ In the case of β -TCDD, the highest Δ_{el} value corresponds to the normal coordinate with the index η , which describes bending of the C–Cl bond in the plane of the molecule (see the letter designations of vibrations in Table 1). In each of these molecules, the highest Δ_{el} value for vibrations involving the benzene fragment corresponds to the normal coordinate Q_k , which is typical of electronic states of the B_{3g} or B_{1u} types (but not A_g or B_{2u}).^{28,30}

Using a simple theoretical model of the Franck–Condon interactions,²⁸ which reflects satisfactorily the experimental Δ_{el} values, the changes in the geometric parameters in the benzene fragments of DD and β -TCDD in the T_1 state have been calculated.^{28,86} It was found that the changes in the lengths of all bonds parallel to the z axis of the molecule [C(2)–C(3) and the three other] are about an order of magnitude greater than the changes in the other bond lengths in the benzene fragments. This is consistent with the results obtained by INDO/S calculations of electronic states (see Fig. 13). The changes in the bond lengths are nearly the same in each molecule and are equal to 0.021 and 0.027 Å for DD and β -TCDD, respectively. In β -TCDD, the C–Cl bonds are rotated in the molecular plane through 0.9°, according to an approximate estimate.³⁹

The intensity of the region in the phosphorescence spectrum associated with the purely electronic transition and with totally symmetric vibrations is determined by the spin-orbit coupling, while the intensity of the other spectral region is governed by the vibronic-spin-orbit coupling.⁷⁵ Determination of the relative intensities of some lines in the spectrum provides⁷⁶ an experimental estimate of the contributions of spin-orbit and vibronic-spin-orbit couplings to the phosphorescence rate constant ($k_{ph} = k_{SO} + k_{VSO}$). The k_{SO}/k_{VSO} values were estimated for the T_1 state of DD, β -TCDD, α,β -TCDD and OCDD molecules.^{39,42,43} The quantitative results obtained^{39,41–43} indicate that an increase in the number of Cl atoms in the molecule (β -TCDD and OCDD) sharply increases the contribution of the vibronic-spin-orbit coupling (with respect to the spin-orbit coupling) to the constant k_{ph} .

The lines corresponding to non-totally symmetric modes do not form progressions if they have originated due to the Herzberg–Teller interactions, *i.e.* if no change in the nuclear configuration of the molecule related to the change of its symmetry typical of the S_0 state is involved. However, apparently, it would be possible to establish correlations between the relative intensities of the vibronic lines caused by Herzberg–Teller interactions and the probable destruction processes of dioxins in photochemical reactions in the electronic state T_1 . For instance, some correlations have been found between the intensity of vibronic lines related to non-totally symmetric vibrations of a particular form and the structural changes in the molecules of carbonyl-containing compounds upon photochemical reactions in the triplet ($\pi\pi^*$) and ($\pi\pi^*$) electronically excited states.⁸⁸

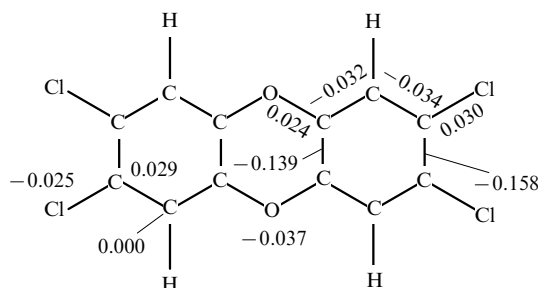


Figure 13. Changes in the electron density on the bonds and atoms of the β -TCDD molecule in the lower triplet excited state $^3B_{1u}(\pi\pi^*)$.⁸⁶ The values for only one of the equivalent atoms are presented.

VI. Spectroscopic analytical investigations

It has been mentioned in the Introduction that dioxins are formed as trace side products in some industrial processes including chemical (production of chlorinated phenols, herbicides and so on) and pulp-and-paper (paper bleaching) processes and during the operation of garbage-incineration plants. This is accompanied by dioxin pollution of the environment. Polychlorinated dibenzo-*p*-dioxins are highly stable compounds. They do not decompose at high temperatures (up to 750 °C); the half-life of PCDD in soil is about 10 years.⁸⁹ Due to their stability, the dioxin toxicants are accumulated in soil, water, plants and animals, which creates hazard for humans and other living organisms, because dioxins are many orders of magnitude more toxic than commonly known poisons (such as potassium cyanide or curare). Realisation of the dioxin menace stimulated the governments of many countries to adopt special programmes on the protection of the environment from these toxic compounds.

One aspect of the environmental protection is the development of highly sensitive methods for determination and quantitative analysis of traces of PCDD. Since dioxins are very hazardous compounds, methods for their analysis should be highly sensitive, at the picogram level. Yet another, equally significant requirement to the methods of dioxin analysis is high selectivity. This requirement originates due to the fact that dioxins having different structures differ markedly in toxic properties.^{4,90,91}

Figure 14 presents the results of an experiment with guinea-pigs. It demonstrates how sharply (by approximately four orders of magnitude) the toxicity of PCDD containing from seven to four chlorine atoms increases as the α -Cl atoms are successively replaced by hydrogen atoms. The effect of PCDD on organisms is appreciably variable; however, generally, the regularity presented in Fig. 14 holds. Thus β -TCDD is considered to be the most toxic.

At present, toxicity equivalent factors (TEF)⁹¹ common to humans and mammals have been established (for β -TCDD, TEF = 1). Apart from β -TCDD, six more PCDD containing four chlorine atoms in the β -positions are considered to be toxic. For example, for 1,2,3,7,8-Cl₅DD and the three isomers of hexachloro-substituted dibenzo-*p*-dioxins, TEF = 1 and 0.1, respectively; for the octasubstituted dibenzo-*p*-dioxin, TEF = 0.0001. Therefore, in monitoring the dioxin contamination, the problem of identification of the most hazardous PCDD is a crucial point. Identification is also important in connection with the need to determine precisely the reason (*i.e.* who is to blame) for the contamination and to control the process of dioxin destruction. From the scientific viewpoint, this is important for determining the mechanisms and the products of destruction of dioxins during incineration, photolysis and chemical or biological deactivation.

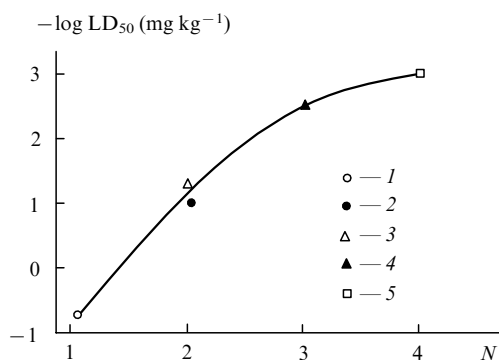


Figure 14. Toxicity of dioxins (the lethal dose LD₅₀ for guinea-pigs) vs. the number (*N*) of hydrogen atoms occupying α -positions in the 1,2,3,4,6,7,8-Cl₇DD (1), 1,2,3,6,7,8-Cl₆DD and 1,2,3,7,8,9-Cl₆DD (2), 1,2,3,4,7,8-Cl₅DD (3), 1,2,3,7,8-Cl₅DD (4) and β -TCDD (5) molecules.²⁴

The best developed and most widely used methods for analysis of dioxins not related to optical spectroscopy include various modifications of the chromatographic method,^{92–95} chromatomass spectrometry,^{96–98} a method combining chromatographic separation of isomers with their NMR detection,⁹⁹ *etc.* Description of all the methods used currently is beyond the scope of this review. We shall restrict ourselves to a brief description of the optical methods of analysis employed for this purpose.

Among optical methods, Fourier IR spectroscopy (FTIR) is used most extensively to analyse dioxins. Usually, this technique is combined with chromatographic methods.⁹⁸ Thus even in the first publications^{32,34} dealing with analysis of dioxins by gas chromatography and FTIR (GC-FTIR method), using reflectance and absorption spectra, the researchers were able to identify all the 22 isomers of tetrachloro-substituted dioxin. This method permits detection of dioxins present in concentrations of several hundreds of nanograms.

A higher sensitivity of the method can be attained by using matrix isolation of the analysed compounds (GC-MI-FTIR).¹⁰⁰ In this case, the isomers separated by chromatography were present in an argon matrix at 12 K; this decreases the line half-width and, correspondingly, increases the peak intensity of lines. The IR spectra of all the 22 isomers of tetrachloro-substituted dioxin were recorded by this method,^{33,35,36} including the spectra of β -TCDD and its completely isotope-substituted analogue ([¹³C] β -TCDD), in which all the ¹²C atoms have been replaced by ¹³C. This technique is suitable for the analysis of samples with contents of tetrachloro-substituted DD of the order of hundreds of picograms.^{36,100,101} For example, the use of [¹³C] β -TCDD as the internal standard permitted determination of β -TCDD in a concentration of 15–45 pg per g in an extract from a fish tissue.³⁷

To identify dioxins on the basis of their IR spectra, several characteristic bands in the range of 1600–800 cm⁻¹ are used.^{24,33,35} Figure 15 presents the IR spectrum of the extract from a fish tissue containing β -TCDD and an internal standard admixed. Generally, the positions of bands in the spectrum recorded by the GC-MI-FTIR method coincide with the positions of the corresponding bands in the spectrum of β -TCDD in a KBr pellet (see Fig. 2).

Figure 16 shows an example of identification, based on IR bands, of two tetrachloro-substituted DD isomers which are poorly resolved by gas chromatography^{102,103} but are separated by gas liquid chromatography. In the frequency range of 1600–800 cm⁻¹, the positions of the maxima of bands in the spectra of these isomers differ only slightly; however, the isomers can be identified based on the different relative intensities of bands. It has also been proposed^{24,35} to identify isomers using the

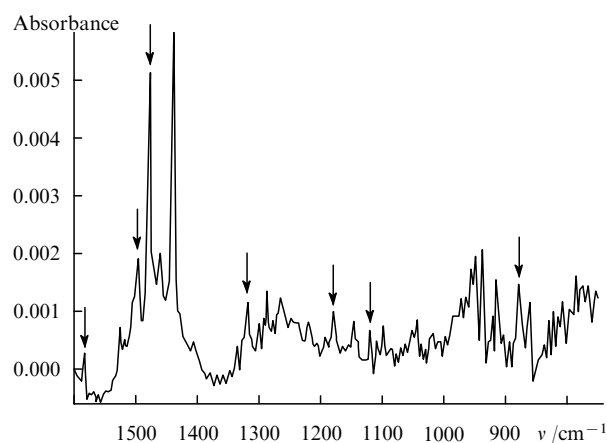


Figure 15. Absorption spectrum of the extract from a fish tissue containing β -TCDD and an admixture of [¹³C] β -TCDD added as the internal standard. The spectrum was recorded by the GC-MI-FTIR technique; the analytical lines of the β -TCDD toxin³⁷ are marked by arrows.

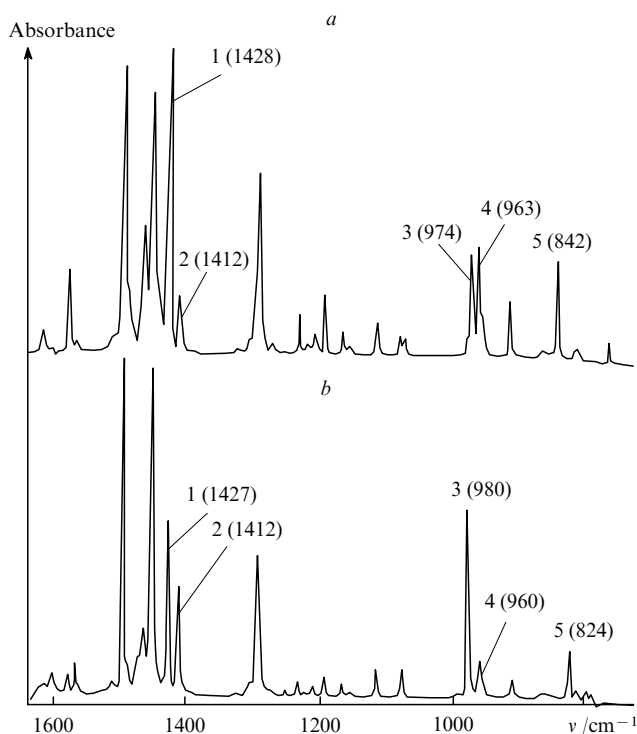


Figure 16. Absorption spectrum recorded by the GC-MI-FTIR method for the isomers 1,2,4,8-Cl₄DD (a) and 1,2,4,7-Cl₄DD (b).³⁵ The numerals 1–5 mark the analytical lines the relative intensities of which at 1420 cm^{−1} (lines 1, 2) and at 980–820 cm^{−1} (lines 3–5) can be used to identify the isomers.

$\nu_{\text{C-O}}^{\text{as}}$ frequencies of the antisymmetric stretching vibrations of the C–O–C groups in the range of 1330–1280 cm^{−1}. However, in our opinion, this spectral region is less reliable for identification because the semiempirical triatomic model considered³⁵ determines the $\nu_{\text{C-O}}^{\text{as}}$ values too crudely; meanwhile, the difference between the experimental values of these frequencies for some pairs of isomers is very little (1–2 cm^{−1}).

The results of identification of PCDD isomers by four independent methods: chromatography, GC-MS, GC-FTIR and ¹H and ¹³C NMR spectroscopy have been compared.¹⁰⁴ For several isomers, the results of identification did not coincide.

It has been proposed^{22,47} to use the frequencies of normal modes of PCDD isomers found theoretically (by *ab initio* calculations) to identify the isomers based on their IR spectra.

Now we shall mention several other spectral methods for determination of dioxins. For example, theoretical estimates of the limits of detection of dioxins by Raman spectroscopy (~2 pg) and by giant Raman scattering (GRS, ~2 × 10^{−4} pg) allow the GRS method to be regarded as a promising analytical technique.¹⁰⁵ A simple photometric method based on the ability of PCDD to be protonated and to form coloured associates with transition metal anions has been proposed.¹⁰⁶ The lower limit of the β-TCDD concentration in a hexane extract determined by this method is 20 pg cm^{−3}.

The detection powers of the setups used in the studies of dioxins by UV absorption and fluorescence methods have been evaluated.^{58,73} Fluorescence of dioxins shows itself as a broad band with a maximum in the region of 330–390 nm. For n-hexane solutions of PCDD containing 5 to 8 Cl atoms, the detection limit of the fluorescence analysis amounts to 0.5–5 ng cm^{−3} at room temperature for excitation with the wavelength $\lambda_{\text{excit}} = 230$ –245 nm.⁷³ This spectrum region contains the maximum of band **B**, the most intense band in the UV absorption of dioxins (see Figs 5, 6). In laser-induced fluorescence analysis of dioxin vapours (β-TCDD, 1,2,3,7,8-Cl₅DD and OCDD) with

$\lambda_{\text{excit}} = 303$ nm and at 170–270 °C, the detection limit was approximately four orders of magnitude lower; it was 0.09–0.13 pg cm^{−3} (see Ref. 58).

The detection power of the setup using the UV absorption method in the short-wavelength region (~224 nm) has been evaluated. The limit of detection of β-TCDD, 1,2,3,7,8-Cl₅DD and OCDD in vapours amounted to 8–90 pg cm^{−3} (see Ref. 58). It is noteworthy that the methods of detection mentioned above are not selective because the UV absorption and fluorescence bands of dioxins are very broad and, moreover, the maxima of these bands shift only slightly upon the change in the number of chlorine atoms in PCDD molecules (see Section IV).

The use of phosphorescence, more precisely, low-temperature quasi-line phosphorescence spectra of solid solutions, for identification of dioxins has also been proposed.^{73,82,85} For example, it is known that the luminescence spectra recorded by this method (Shpol'skii method) have been used successfully to determine the content of polycyclic aromatic hydrocarbons as hazardous contaminants in foodstuffs and in non-edible oils.^{107,108} The phosphorescence spectra of solid solutions of DD and many of PCDD in a 1 : 5 : 5 mixture of ethanol, isopentane and ether⁷³ at 77 K and in n-alkanes at 77 and 4.2 K^{81,82,85} were shown to possess a quasi-line structure, the structures of spectra of different PCDD being substantially dissimilar (see Table 6). The differences are observed both in the positions of lines and in the intensity distribution. Thus, these spectra possess advantages over the structureless UV absorption and fluorescence spectra in the identification of compounds.

Figure 17 presents the phosphorescence spectrum (4.2 K) of a mixture of β-TCDD and α,β-TCDD isomers with concentrations

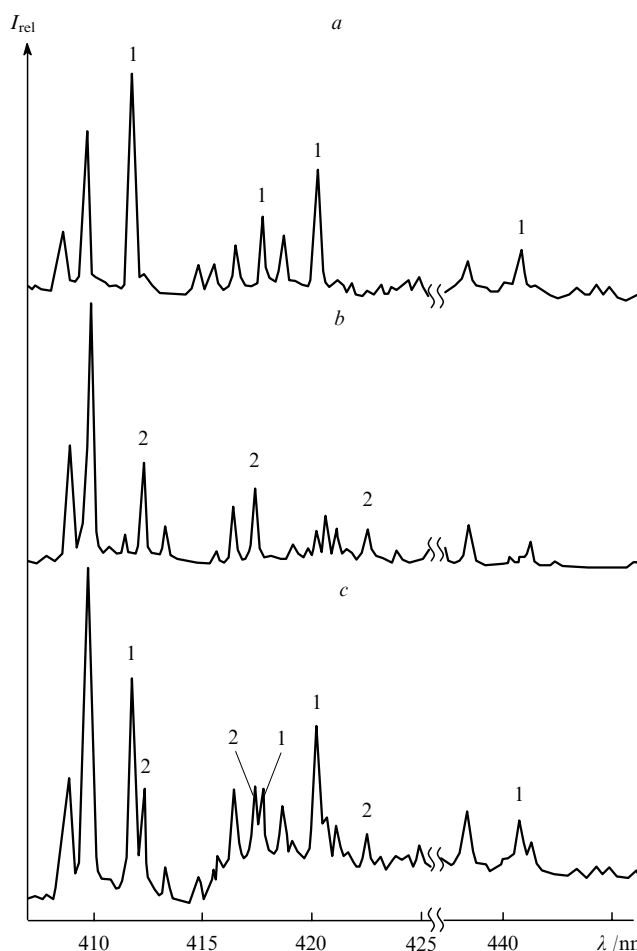


Figure 17. Phosphorescence spectra of α,β-TCDD (a), β-TCDD (b) and their mixtures (c) in n-hexane at 4.2 K.⁸² In spectrum c, the analytical lines 1 and 2 corresponding to the two isomers (a and b) are marked.

of 4.5×10^{-5} and 3×10^{-5} mol litre $^{-1}$, respectively. The quasi-lines observed in the emission spectrum of a two-component solution can be assigned unambiguously to one of the mixture components, which is a clear illustration of the possibility of selective determination of isomers using these spectra. At 77 K, the phosphorescence spectra of PCDD isomers are less suitable for selective recording due to the greater ($\sim 2-4$ nm) half-width of bands. However, the simplicity of the equipment and the process of recording provides the possibility of developing a screening method for dioxin detection based on them.

The detection capacity of the spectral setups used for the detection of dioxins on the basis of quasi-line phosphorescence spectra has been evaluated.^{73, 81, 82} At 77 K, for n-hexane solutions of dioxins containing 4 to 7 Cl atoms, the detection limit is 1–12 ng cm $^{-3}$ (see Ref. 73). The spectra of β -TCDD were found to be recorded reliably down to a concentration of 16 ng cm $^{-3}$ (see Ref. 82). When analysing microvolumes of β -TCDD with recording of the most intense line in the spectrum ($\lambda = 410$ nm, see Table 6), determination of its amounts not lower than 100 pg is possible. It is expected that the limit of detection of tetrachloro-substituted DD could be markedly decreased by decreasing the temperature to 4.2 K, due to the increase in the peak intensity of vibronic lines.

The differences between the quasi-line phosphorescence spectra even for isomers with close structures and for PCDD with different numbers of Cl atoms gives hope that development of such a method would allow reliable identification of PCDD in complex mixtures.

VII. Conclusion

Since it is the molecular structure that accounts for the different photophysical properties of compounds, it is important to establish the geometrical structure of dioxins. X-Ray diffraction data point to a planar or nearly planar structure of DD and PCDD molecules in the crystals. No direct experimental data on the structures of these molecules in the gas phase or in solutions are available to date. Only indirect methods of determination do exist, relying on the data on the dipole moment of DD in solutions or on the results of theoretical calculations. Depending on the theoretical method of modelling employed, the equilibrium nuclear configuration of the molecule in the ground electronic state S_0 is found to be either planar or non-planar. In the case where the dioxin molecules are found to be non-planar, some researchers concluded that, in particular, DD has a 'butterfly' configuration. Data on the structures of dioxin molecules are contradictory. Some investigators who give credit to X-ray diffraction data believe that the dioxin molecules are planar; other researchers who rely on calculations consider that the molecules are non-planar. Note that the intramolecular vibration mode of the 'butterfly' type shows itself at a low frequency for all dioxins. Dioxin molecules might occur in different configurations depending on the experimental conditions (temperature, intermolecular interactions).

In some studies, attempts are made to relate different toxicities of PCDD to either planar or non-planar geometrical configuration. Spectroscopic methods of investigation are especially promising for the solution of the problem of the structure of dioxins (at least, four of them, DD, β -TCDD, 1,4,6,9-Cl $_4$ DD and OCDD) which belong to the D_{2h} group of symmetry in the case of a planar configuration. Analysis of the IR and Raman spectra from the standpoint of selection rules could promote solution of the problem of the molecular configuration in the ground electronic state S_0 . This type of analysis of the fine vibrational structure of the spectra recorded by electronic-vibrational spectroscopy methods (low-temperature UV absorption, hole burning, fluorescence, phosphorescence, excitation of luminescence) and by the resonance enhanced two-photon ionisation technique could facilitate solution of the problem (which has not yet been solved either) of the symmetry of the dioxin molecules in the S_1 and T_1 states.

However, no comprehensive experimental and theoretical studies of dioxin vibrations that could answer the questions about the molecular configuration have been reported so far.

In view of the foregoing, one of the most important problems in the studies of dioxins is to investigate the intramolecular vibrations (both theoretically and experimentally). At present, almost no data on the Raman spectra are available. Despite the extensive use of IR spectroscopy for analytical purposes, data on low-frequency vibrations can scarcely be found in the literature. The results on the theoretical calculations that provide information on not only the frequencies but also the forms and types of symmetry of vibrations are also few. The data on the vibrations of dioxin molecules are also important for the interpretation of the fine vibrational structure of the electronic-vibrational spectra, in particular, phosphorescence spectra of solid solutions because the structure of these spectra is complicated by the presence of the Shpol'skii multiplet components. Interpretation of the vibrational structure of these spectra provides valuable information on the type of symmetry of the triplet electronic state, on the influence of chlorine atoms on the processes of photophysical deactivation of the electronically excited state and on the changes in the nuclear configuration of the molecule in this state.

Fourier Transform IR spectroscopy with matrix isolation of the molecule (combined with chromatography) is currently the main spectral method used to detect and identify dioxins. We believe that the Shpol'skii method would become yet another technique for the detection and identification of dioxins (at present, it is used for polycyclic aromatic hydrocarbons), provided that the light-gathering power of the equipment would be increased somewhat, for instance, by using FT spectrometers. At present, the results of investigation of the fine-structure phosphorescence spectra of solutions of dioxins in non-branched alkanes at 77 and 4.2 K (using a standard spectrometer with diffraction gratings) confirmed the good prospects for using this technique for analytical purposes as a highly sensitive and selective method.

The knowledge of experimental photophysical characteristics of dioxins and their changes induced by particular factors (medium, temperature, *etc.*) is required not only for theoretical investigations of the mechanisms of deactivation of electronic states but also for the solution of some practical problems. Thus it is known that photochemical decomposition, which is supposed to proceed through a T_1 state, is the most effective process for the destruction of these toxicants. However, the available data on the photophysical studies of dioxins are obviously insufficient to provide optimisation of the methods for their photochemical deactivation. These data are also needed for searching for the ways of increasing the sensitivity of the spectral luminescence methods of analysis.

New data on the structure and properties of dioxins would help to disclose the mechanism of action of these ecotoxins; they would enable further development and perfection of both analytical methods for the detection of dioxins and methods of environmental protection.

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^h — *Russ. J. Struct. Chem. (Engl. Transl.)*

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Preparation of thin copper films from the vapour phase of volatile copper(I) and copper(II) derivatives by the CVD method

V N Vertoprakhov, S A Krupoder

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Abstract. The main chemical aspects of the preparation of thin copper films from the vapour of monovalent and divalent copper derivatives as precursors in the CVD technique are considered. Data on the methods of synthesis and the properties of various types of these compounds are generalised and described systematically. The possible decomposition mechanisms of copper compounds under CVD conditions are discussed. The prospects of using the CVD technology for the preparation of thin copper films in integrated circuits of microelectronic devices are outlined. The bibliography includes 432 references.

I. Introduction

Micro- and nanoelectronics are the most promising fields for the application of thin copper films. Such films are used as conducting paths in large-scale and very-large-scale integrated circuits (LIC and VLIC, respectively); they make an alternative to aluminium films. It is known that non-doped aluminium films used as electric wiring in LIC and VLIC have a number of drawbacks. First, discontinuity of aluminium films is observed during operation of integrated circuits because of the large atom electromigration coefficient, which was shown by calculations to be due to relaxation of the bulk upon passage of a flow of vacancies.¹ On the other hand, the electromigration coefficients in the layers of copper atoms are a few orders of magnitude smaller than in aluminium atom layers. Second, the specific electric resistance (SER) of copper is 30% smaller than that of aluminium. The addition of copper or silicon (2 at.%–4 at.%) to aluminium films does not eliminate all the drawbacks of aluminium as a material for interconnections in LIC and VLIC.^{2–9}

In addition, thin copper films are used in devices which employ the effect of the gross magnetic resistance in polycrystalline Co/Cu multilayers. The thickness of the cobalt and copper

layers ranges from a few fractions of a nanometre to several nanometres.^{10–14}

Copper films are deposited onto substrates. Silicon and silicon dioxide are the most common substrate materials. The diffusion coefficients of copper into silicon and silicon dioxide are high, they are a few orders of magnitude higher than those of other metals. The use of barrier layers in order to decrease this coefficient was suggested. At first, it was attempted to solve this problem by means of PVD (Physical Vapour Deposition) technology, using such methods as thermal evaporation, plasma spraying, magnetron or laser scattering, as well as by spray deposition of thin layers of other metals (Cr, Co, W, Ti, Ta) on an SiO₂ surface. However, little progress has been made in this direction. Later, metal nitrides used as the barrier layer materials showed better performance than the pure metals.

The common drawback of PVD technology is the necessity of heating a substance to high temperatures (above the vaporisation temperature). Therefore, intense development of CVD (Chemical Vapour Deposition) technology has started in recent years; this technique involves chemical methods of deposition of thin films from the gas phase using metal-containing compounds. Chemical methods have a number of advantages over physical methods. These include relatively mild conditions for film deposition, comparatively low vaporisation temperatures of the starting compounds, conditions favourable for good adhesion of the films to the substrate, wider technological prospects for the development of microelectronic devices with required parameters.

This review considers the chemical methods used in CVD technology for the preparation of copper films from volatile copper(II) and copper(I) derivatives. The main attention is given to work published within the period from 1991 to 1999, although earlier fundamental studies have also been taken into account.

The majority of compounds which we name 'copper-containing compounds' (CCC) correspond to copper complexes with copper–oxygen bonds. As to the specific CCC types, the review mentions virtually all classes of compounds considered as promising starting compounds for CVD technology. Many of these compounds have not yet found application in the synthesis of copper films. Nevertheless, we felt it worthwhile to mention them as well, at least because it is quite possible that other CCC of the same classes may be suitable for CVD processes.

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II. Equipment used in CVD processes

A vast literature (see, *e.g.*, Refs 15–28) is devoted to CVD technology. In essence, the CVD process involves evaporation of volatile metal-containing compounds followed by transfer of their vapour to a reaction compartment, where the starting compound is decomposed and the decomposition products are deposited onto a substrate in the form of a film. Most commonly, decomposition is accomplished by means of thermolysis, sometimes along with exposure to plasma or irradiation. Side products are removed from the reaction zone in the form of vapour.

If the process is carried out with the use of an inert gas as the carrier for the vapour of the starting compound, it is usually purified from oxygen and other admixtures by passing it preliminarily through adsorbents or a membrane. Hydrogen is purified by passing it through palladium.²⁹ Liquid compounds are injected using devices based on controlling the mass consumption rate.^{30, 31}

Various designs of reactors have been developed for the CVD processes.[†] As an example, Fig. 1 shows a simple reactor scheme for pyrolytic deposition of films by evaporation of metal-containing compounds followed by transportation of the vapour to the deposition zone.

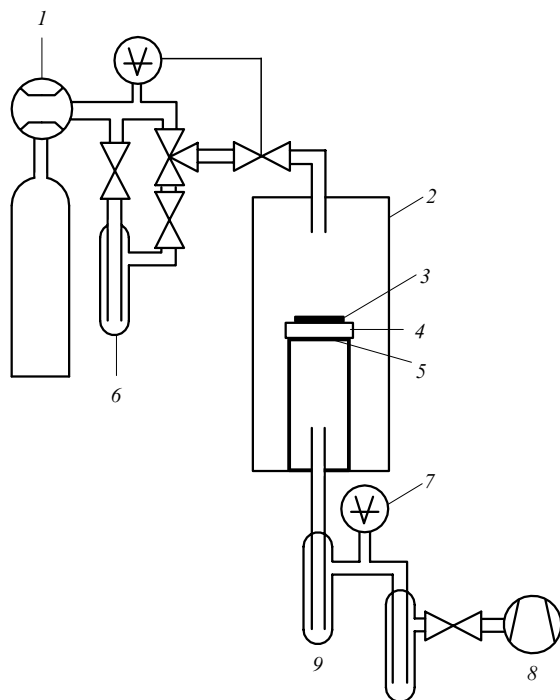


Figure 1. The simplest CVD reactor scheme;⁴⁰ (1) flow controller, (2) reactor, (3) substrate, (4) heater, (5) thermocouple, (6) CCC source, (7) manometer, (8) pump, (9) liquid nitrogen trap.

Many reactor designs and film deposition processes have been patented.^{35, 41–44} A number of firms manufacture serial reactors, *e.g.*, MR-200 (Cambridge Instruments, Great Britain),⁴⁵ EMCORE (GS/3300 firm, USA) with a rotating disk and uniformity of the substrate temperature to within 1 °C,⁴⁶ EPISON (Thomas Swan Ltd, Great Britain).^{47, 48}

[†]They can arbitrarily be divided in two groups: vertical^{32–35} and horizontal.^{35–39} A review of the equipment used before 1972 for the deposition of films and coatings by CVD can be found in Ref. 15 (see p. 180 *ff*).

High-performance technological equipment for the preparation of thin layers by CVD has been developed at the Samsung company's institute (Republic of Korea). This equipment makes it possible to manufacture more than 10 000 devices (diodes, photo diodes, *etc.*) simultaneously.³⁶

The design of a CVD reactor in which hydrogen plasma is used was reported.⁴⁹ High-quality copper films with a SER of 2.0 $\mu\Omega$ cm are obtained in such reactors.

In recent years, combined instruments (of the so-called cluster type) for the deposition of any type of thin films by physical or chemical methods, including CVD technology, have appeared (see, *e.g.*, Ref. 50). These instruments allow one to deposit multi-layer coatings from different materials.⁵¹ An example of such an instrument is shown in Fig. 2.

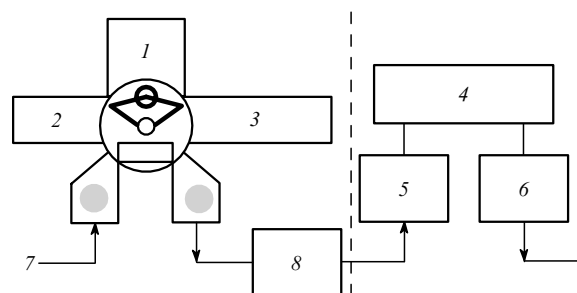


Figure 2. Block diagram of a 'cluster' apparatus for the preparation of thin films;⁵²

(1, 2) process modules, (3) observation module, (4) multifunctional module (exposure, polishing, *etc.*), (5) sample preparation module, (6, 8) measuring modules, (7) support inlet.

CVD methods are successfully used if high-quality and uniform films (both with respect to the composition and thickness) of large area are required. For this purpose, the substrates in the reactor are rotated; laminar gas streams in the reactor and uniform heating are provided. In this way, thickness uniformity within 2% and chemical composition uniformity within 1% can be achieved over the entire film surface.^{53–56} Visualisation of convective flows in the growth chamber can be provided by laser illumination of dispersed particles or by creation of a 3D image by interference holography.

The production of integrated circuits requires the preparation of planar deposited copper layers. For this purpose, the technology of chemical and mechanical polishing of copper films has been developed which includes treatment of the film surface with a suspension of fine SiO_2 and Al_2O_3 particles; benzotriazole is added as an oxidant if necessary. In the latter case, the rate of film surface polishing depends on the concentration of benzotriazole.^{57, 58}

The waste gases are utilised using catalytic combustion, physical adsorption with activated carbon with or without oxidation and dry purification in reaction columns.^{59, 60} The CS-GmbH company (Germany) has developed three types of gas absorbents: absorbing cartridges (Cleanvent), washing and purifying systems (Cleantorb) and emergency absorption systems (Clean-Protect). The Cleanvent cartridges are intended for *in situ* removal of hazardous gases from gas distribution systems.⁶¹

III. Barrier layers preventing the diffusion of copper atoms into the substrate

Diffusion of copper atoms into the substrate during the operation of microelectronic devices impairs their characteristics. This can be prevented by means of barrier layers between the copper film and the substrate. These layers consist of certain metals and/or binary compounds and can be obtained using PVD or CVD

technologies. CVD favours the formation of amorphous films, as shown, *e.g.*, for tantalum nitride.⁶²

1. Barrier layers prepared by PVD methods

Originally, diffusion of copper atoms into silicon as the most common substrate was prevented by thin barrier layers of diamond-like carbon and metal films obtained by PVD methods.^{63, 64} Films of various binary compounds, primarily titanium, tungsten and tantalum silicides, borides and nitrides, are also suitable for this purpose.^{65–85}

Tungsten and tantalum are regarded as the best metals for the deposition of barrier layers by PVD, as they have the smallest self-diffusion coefficients in the series $Ti > Cr > Nb > Mo > Ta \sim W$.⁶⁴ After deposition, the layers are exposed to annealing in hydrogen for 1 h at 600 °C.⁶⁴

Metal film barrier layers were gradually replaced by films of titanium and tungsten silicides and nitrides.^{65–74} In this case, the thermal stabilities of the layers increased to 500 °C (WSi_x multilayer)⁶⁸ and 700 °C (WSiN/WSi_x/W multilayer).⁶⁹ The layers of solid solutions of titanium in tungsten, TiW (30 at.% Ti), have somewhat different characteristics. If the barrier layers are 100 nm thick, the Cu/TiW/Si multilayers are stable up to 775 °C, and their stabilities increase to 850 °C upon keeping in air. In the latter case, 0.2 at.% of oxygen was detected in the film.⁷²

The pure tantalum film 10 nm thick is an efficient barrier against the diffusion of copper into the silicon substrate up to 500 °C.⁶⁹ The films of tantalum nitrides, *viz.*, Ta₂N, TaN, and those of the Ta₃₆Si₄₄N₅₀ alloy provide even more reliable protection against penetration of copper atoms into the silicon substrate.^{75–77, 79, 82} The characteristics of barrier layers are listed in Table 1.

2. Barrier layers prepared by the CVD method

The compositions and properties of barrier layers obtained by thermolysis using the CVD technology depend both on the

conditions of the process and on the properties of the starting volatile compounds.

Generally, the CVD method allows one to work with a wide range of starting volatile compounds of metals (for example, 15 starting volatile compounds have been listed⁷⁸ for the preparation of just one compound, TiN); layers with required properties can be obtained by varying the process parameters (vapour phase composition, deposition temperature, pressure).

Table 2 lists the starting compounds and some characteristics of CVD processes for the preparation of thin barrier layers of TiN, TaN, Ta, Ti, Cr, and Co.

It should be noted that PVD methods for the preparation of thin layers from the gas phase (spraying of compounds by bombardment with high-energy electrons and ions, magnetron and radio-frequency spray deposition, *etc.*) require that higher energy was applied to the substance for evaporation. The growth of films generally starts with the formation of separate islets-droplets, which subsequently merge to form a continuous film. Polycrystalline films are mostly formed; this is undesirable in terms of the diffusion of copper atoms, as the grain boundaries have higher diffusion coefficients than the grain bulk.

On the other hand, CVD of compounds from the gas phase generally occurs at lower temperatures. In this case, amorphous films are formed. The diffusion coefficients of copper atoms through the bulk of such films are smaller than through the grain boundaries. This is one of the advantages of chemical methods for film deposition from the gas phase over physical methods.

Yet another advantage of CVD methods is the possibility of selective processes, *i.e.*, preferential deposition, in particular of copper, on one substrate material or surface area with certain mechanical characteristics with respect to another material or surface area. This is a very useful feature for the production of microelectronic devices, as it can replace lithographic template preparation in the creation of an integrated circuit.

Table 1. Parameters of barrier multilayers preventing the diffusion of copper atoms into the silicon substrate.

Multilayers	Deposition method	<i>l</i> /nm	<i>T</i> ₁ /°C	<i>T</i> ₂ /°C	Ref.
Cu/(DLC)/Si	PECVD	100	400	—	63
Cu/M/Si, M = Cr, Ti, Nb, Mo, Ta, W	CVD	60	600	—	64
Cu/Cr/Si	"	10–40	400	500	65
Cr/Cu/Co/Au	"	320	400	500	66
Cu/CrN _x /Si	"	50	70	800	67
Cu/Cr/Si	"	50	500	—	67
Cu/WSi _x /Si	PACVD	50	500	550	68
Cu/WSiN/WSi _x /W/Si	"	450	650	650	69
Cu/WSiN/WSi _x /Si	"	50	500	650	70
Cu/TiB ₂ /Si	LPCVD	150	650	—	71
Cu/TiW/Si	PECVD	100	775	850	72
Cu/TiW/Al/SiO ₂ /Si	PVD	50/100	450/500	—	73
Cu/TiN/Si	LPCVD	40	450	—	74
Cu/TiN/Si	CVD	50	550	—	83
Cu/TaN/Si	PVD	180	500	950	75
Cu/TaN/Si	"	—	—	800	78
Cu/TaN/SiO ₂ /Si	"	25/10	700/600	800	81
Cu/Ta ₂ N/Si	"	50	550	700	77
Cu/Ta/Si	"	20	320–630	630	80
Cu/Ta + CeO ₂ /Si	"	—	800	—	84, 85

Note. The following designations are used: *l* is barrier layer thickness; *T*₁ is the upper limit of the stability temperature range; *T*₂ is the annealing temperature where new phases are formed; DLC is diamond-like carbon; PACVD is plasma-activated CVD method; LP is low pressure.

Table 2. Process parameters for CVD deposition of TiN, TaN, Ti, Ta, Cr and Co barrier layers.

Starting compound	$T/^{\circ}\text{C}$	$T_g/^{\circ}\text{C}$	Carrier gas	P/Torr	Substrate	Ref.
$\text{Ti}(\text{NMe}_2)_4$	—	100–500	NH_3	1–20	Si	86, 87
	45	350 ^a	He, N_2 , Ar	1	SiO_2/Si	88
	60	200–450	Ar	0.8–5	SiO_2/Si	89
	—	300–580	NH_3	—	—	84
	—	377	NH_3	—	TiSi_2 , Al, Cu	90
	—	300–350	NH_3	2–7.5	InP	75
	—	250–500 ^a	N_2 , H_2 , NH_3	0.5–5	Si	87, 91
	—	425	Ar, NH_3	10	Si	92
	—	300–580	NH_3	—	Si	93
	—	425	NH_3	10	Si	92
$\text{Ti}(\text{NEt}_2)_4$	40–50	425	N_2	0.2	Si	94
$(\text{Bu}_2\text{N})\text{Ta}(\text{NEt}_2)_3$	—	450–650	H_2 , N_2 , NH_3	—	Si	95
$\text{CpTi}(\text{C}_7\text{H}_7)$	—	300–600 ^a	H_2 , N_2 , NH_3	—	Si	96
$(\text{Cp})_2\text{Ti}(\text{N}_3)_2$	—	350 ^b	N_2	—	Si	97
$\text{Ti}(\text{OPr}^i)_4$	—	500–550	N_2 , H_2	—	steel	98
$\text{Ta}(\text{NEt}_2)_5$	285	350–400	—	—	—	99
Ar_2CrI	80–82	320	—	—	—	100
$(\text{C}_6\text{H}_5\text{COOEt})_2\text{Cr}$	25–35	260	—	—	—	101, 102
$\text{Co}_2(\text{CO})_8$	—	200–300	H_2	0.01–0.1	SiO_2 , Si	103
CpCoEt_2	—	240–400	H_2	—	SiO_2 , Cu, Al	104
$\text{Co}(\text{acac})_2$	—	320–350	—	—	glass	104
$\text{Co}(\text{acac})_3$	—	320–350	—	—	"	104
$\text{Co}(\text{CO})_3\text{NO}$	—	350–480	Ar, H_2	1.5	SiO_2/Si	105

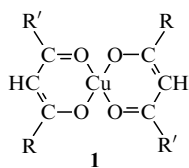
Note. The following designations are used: T is the vaporisation temperature of the compound; T_g is carrier gas temperature; P is pressure in the reactor.

^a In plasma. ^b Under UV irradiation.

IV. The starting copper-containing compounds: copper(II) derivatives

Volatile copper(II)-containing compounds had been synthesised long before the CVD technology appeared. Of these, chelate complexes of copper(II) with β -diketones **1** have been studied most thoroughly.

Copper(II) acetylacetonate, $\text{Cu}(\text{acac})_2$ (**1**, $\text{R} = \text{R}' = \text{Me}$) synthesised in the past century,¹⁰⁶ was the first compound of this series which may be regarded as an appropriate volatile CCC for CVD. By the early 1960s, the number of copper(II) β -diketonates with various starting β -diketones exceeded sixty.^{107–109}



Initially, the application of these compounds was limited to their use as convenient labels for characterisation of the corresponding β -diketones and in gas chromatography for the separation of metals.¹⁰⁹ As a matter of fact, the use of copper β -diketonates in CVD technologies began in 1965 when the first study devoted to the CVD synthesis of thin copper films based on β -diketonates appeared.¹¹⁰ To date, there are several reviews dealing with copper β -diketonates as volatile CCC (see, for example, Refs 26 and 111), but they did not cover the work published in recent years.

Certainly, not all copper(II) β -diketonates and their derivatives are suitable for CVD processes. The synthetic accessibility of the starting β -diketone is of certain importance, but the practical value of a particular copper(II) β -diketonate is determined by the combination of its physicochemical properties.

The relationship between the volatilities of metal β -diketonates (including that of copper) and their structures was analysed by Mazurenko *et al.*^{112, 113} (see also the review by Tsyganova and Dyagileva¹¹⁴). The main criteria of stability of these compounds in the vapour phase have been stated in these reports. It is

believed¹¹³ that the rather high volatilities of these compounds are due to shielding of the coordination unit by the highly developed 'periphery' of the molecules, which decreases the contributions of the electrostatic and intermolecular interactions to the intermolecular potential.

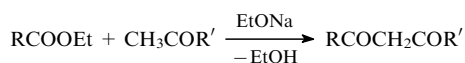
However, volatility is a necessary but insufficient condition for the applicability of compounds in CVD technology. The basic requirements to the starting CCC are as follows:¹¹³ the ability to undergo sublimation in low vacuum at as low temperatures as possible, providing as high a vapour pressure as possible; the ability to undergo sublimation and resublimation without decomposition; the ability to undergo thermolytic decomposition on a substrate surface at as low a substrate temperature as possible with a minimum possible content of admixtures in the resulting copper film.

Analysis of these requirements makes it possible to conclude that the thermolytic stability of the starting compound should have an optimum. In the best case, an insufficiently stable compound will reach the substrate surface as decomposition products, which is unfavourable for reproducibility of the process. If the compound is very stable, high substrate temperature (or additional energy in the form of radiation) is inevitably required for thermolysis, which generally affects adversely the film quality.

The starting volatile copper(II) derivatives with optimum technological properties for the CVD method have been sought among several basic groups of compounds considered below.

1. Copper(II) β -diketonates with alkyl groups

The main advantage of copper(II) β -diketonates with alkyl groups is their synthetic accessibility. However, they were not the first compounds used for the development of the CVD preparation of copper films; their polyfluorinated analogues were the first substances.^{110, 115, 116} This is most probably due to the rather low volatilities of this type of copper(II) β -diketonates.¹¹⁷ The β -diketonates required for the preparation of metal β -diketonates can be synthesised rather easily by the Claisen condensation of the corresponding ketones with esters in the presence of nucleophilic reagents.¹¹⁸



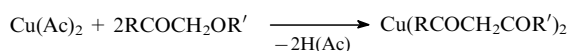
The suitability of copper(II) acetylacetonate $\text{Cu}(\text{acac})_2$ and copper(II) dipivaloylmethanate $\text{Cu}(\text{DPM})_2$ in CVD processes was considered. The latter compound is more volatile than $\text{Cu}(\text{acac})_2$ because the β -diketone has a branched hydrocarbon chain (see **1**, $\text{R} = \text{R}' = \text{Bu}^t$).¹¹⁶

Substituted copper(II) acetoacetates¹¹⁷ (Section IV.4a) provide an alternative to these compounds in the hydrocarbon series.

a. Synthesis and physicochemical properties

The main method for the synthesis of $\text{Cu}(\text{acac})_2$ and other copper(II) β -diketonates with alkyl groups involves the reaction of the corresponding β -diketone or its hydrate with a hot aqueous solution of copper(II) acetate¹¹⁹ or a mixture of a water-soluble copper(II) salt with sodium acetate.¹²⁰ Copper β -diketonate hydrates are usually obtained in this way; anhydrous compounds are obtained by heating or by keeping the hydrates over H_2SO_4 .¹²⁰ It was noted, however, that the formation of a hydrate is untypical of $\text{Cu}(\text{acac})_2$.¹²¹

Direct reaction of copper(II) acetate with an anhydrous β -diketone, which occurs in several minutes in boiling β -diketone, is also possible.¹¹⁹



The structure and spectral properties of the simplest β -diketonate, *viz.*, $\text{Cu}(\text{acac})_2$, have been studied rather thoroughly: all bond lengths and bond angles in the $\text{Cu}(\text{acac})_2$ molecule have been determined;¹²² quantum-chemical calculations of the electronic structure of $\text{Cu}(\text{acac})_2$ have been carried out;^{123,124} the ESR spectra of this compound have been recorded (see, *e.g.*, Refs 125 and 126); a detailed assignment of its IR spectral bands has been performed.¹²⁷

When deciding whether a compound can be used in CVD, its molecular structure and thermogravimetric data are of special importance. It was shown that in $\text{Cu}(\text{acac})_2$ and other copper(II) β -diketonates, the separate molecules form infinite chains through intermolecular copper–chelate ring carbon bonds^{128,129} with a bond length of 0.301–0.312 nm. This interaction complements the coordination of copper atoms to give a strongly stretched tetragonal bipyramid. The relative instabilities of these intermolecular bonds can be a reason for the volatility of this class of compound.¹¹³

The thermodynamic parameters of the $\text{Cu}(\text{acac})_2$ molecule are listed in Ref. 130. The vapour pressures of this compound were measured at various temperatures (for example, it is ~ 0.3 Torr at 150 °C) and the temperature dependence of the vapour pressure was obtained.¹³¹ It was shown by thermogravimetry that $\text{Cu}(\text{acac})_2$ is sublimed completely and does not undergo decomposition in an inert atmosphere.¹³² On the other hand, the results of thermogravimetric analysis of $\text{Cu}(\text{acac})_2$ in air suggest that a single-step thermal decomposition occurs at 305 °C.¹³³ The usual temperature range of $\text{Cu}(\text{acac})_2$ sublimation in a CVD process is 100–170 °C.¹³⁴

Dipivaloylmethane $\text{H}(\text{DPM})$ and $\text{Cu}(\text{DPM})_2$ were first obtained by condensation of ketones with esters in the presence of NaNH_2 .¹²¹ Simpler methods for the synthesis of $\text{Cu}(\text{DPM})_2$, *e.g.*, the reaction of $\text{H}(\text{DPM})$ with an aqueous solution of CuSO_4 in the presence of sodium acetate, were developed later.¹³⁵ The properties of $\text{Cu}(\text{DPM})_2$ have also been studied rather thoroughly: the crystal structure has been determined;¹³⁶ thermogravimetric data have been obtained showing that in a nitrogen atmosphere $\text{Cu}(\text{DPM})_2$ sublimates completely at 240–245 °C;^{131,132} its sublimation enthalpy (74.8 kJ mol⁻¹) and entropy (132.2 J mol⁻¹ K⁻¹) have been determined.¹³⁵ Analysis of thermogravimetric curves for a wide range of copper(II) β -diketonates with alkyl groups^{131,132} showed that

$\text{Cu}(\text{DPM})_2$ is actually the most volatile compound in the series where both ligands are identical (the compounds with different ligands are less accessible synthetically).

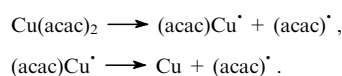
b. The mechanisms of decomposition of copper-containing compounds on substrate surfaces

The mechanisms of formation of copper films from copper(II) β -diketonates with alkyl groups in CVD processes have been studied in various respects. A number of studies (see, *e.g.*, Refs 137, 138 and references cited therein) deal mainly with the physical aspects of the growth of copper films and its mathematical simulation.

Turgambayeva *et al.*^{139,140} used mass-spectrometric data to analyse the thermolysis of $\text{Cu}(\text{acac})_2$ molecules in the vapour phase in a vacuum as well as in a stream of oxygen and hydrogen. It was shown that, depending on the temperature, thermolysis can result in various volatile organic products, such as $\text{H}(\text{acac})$, acetone, ethyl methyl ketone, *etc.* The kinetic and activation parameters of the thermal decomposition of $\text{Cu}(\text{acac})_2$ in the vapour phase were reported;^{140,141} this process was described satisfactorily by a first-order kinetic equation. It was concluded on the basis of IR spectra of $\text{Cu}(\text{acac})_2$ that the decomposition starts with destabilisation of the coordination unit at the copper–oxygen bonds of the complex.¹⁴² A similar study of the kinetics and thermal decomposition products in the vapour phase was also carried out for $\text{Cu}(\text{DPM})_2$.¹⁴³

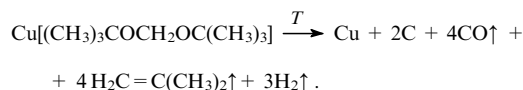
It is very important to have data on the mechanism of thermolytic decomposition of compounds directly on the substrate in order to bring the CVD processes to perfection.

One of the first schemes suggested for the description of $\text{Cu}(\text{acac})_2$ decomposition on heated substrate surfaces involved a radical mechanism:¹⁶



It is considered that subsequent decomposition of the acetylacetone radical will produce contaminants (admixture of carbon and copper oxides) in the film.

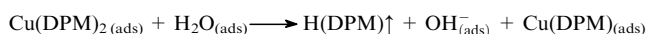
A somewhat different scheme of $\text{Cu}(\text{DPM})_2$ decomposition is described in Refs 144–146. A study of the thermolysis mechanism by *in situ* Fourier IR spectroscopy at a substrate temperature of 500 °C and a pressure of 20 Torr showed that the process starts with the cleavage of the C–C bonds of the chelate ring accompanied by simultaneous partial elimination of the *tert*-butyl groups. As a result, isobutene is formed. The thermolysis is abruptly accelerated at 600–700 °C; the films formed at temperatures above 600 °C are considerably contaminated with carbon. The overall decomposition equation is:



The interaction of $\text{Cu}(\text{DPM})_2$ with a substrate surface was studied by IR spectroscopy during the decomposition of the vapour in the presence of H_2O on the (100) planes of SiO_2 crystals (see Refs 147 and 148) and SrTiO_3 crystals (see Ref. 149) with formation of a copper film.

It was shown that the film formation on the SiO_2 surface starts with stoichiometric chemisorption of the copper(II) β -diketonate involving reactive surface OH groups. This reaction occurs even at 50 °C and results in the disappearance of the peak assigned to OH groups in the IR spectrum.¹⁴⁸ It was found that one $\text{Cu}(\text{DPM})_2$ molecule at the surface is coordinated with two or three OH groups.

In the presence of water vapour providing adsorbed water on the substrate or upon direct participation of OH group protons, decomposition of $\text{Cu}(\text{DPM})_2$ with elimination of one $\text{H}(\text{DPM})$ molecule and formation of copper(I) dipivaloylmethanate $\text{Cu}(\text{DPM})$ occur, as confirmed by XPS data.



As shown in more detail for polyfluorinated analogues (see Section IV.2.b), the intermediate copper(I) compound can undergo both reduction and disproportionation to give metallic copper and the original copper(II) compound.

This reaction on the SiO₂ surface also gives copper(I) oxide.¹⁴⁷

Deposition of copper onto the SrTiO₃ substrate was preceded by bombardment with Ar⁺ ions giving Ti³⁺ ions in the near-surface layer, which favoured the adsorption of the H₂O molecules. The mechanism of Cu(DPM)₂ transformations on the SrTiO₃ substrate is similar to that described above for the SiO₂ substrate.¹⁴⁹

Improvement of copper film characteristics in the CVD process based on copper(II) β-diketonates with alkyl groups, in particular a decrease in the SER, is reached under additional UV irradiation. Zama *et al.*¹⁵⁰ believe that in this case, UV irradiation favours the migration of the copper atoms over the growing copper film surface, thus decreasing the grain size and, hence, producing a smoother surface.

c. Preparation and characteristics of copper films

The use of copper(II) acetylacetonate as the starting CCC for the preparation of thin copper films by CVD began in the early 1990s,^{134, 151} though some earlier works on this process (mostly patents) are known (see Ref. 16).

A study of CVD of copper films from Cu(acac)₂ vapour onto a SiO₂/Si substrate at 220–250 °C (with an argon–hydrogen mixture as the carrier gas) showed that the structure and morphology of copper films are primarily determined by two factors, *viz.*, the deposition rate and the partial pressure of hydrogen in the carrier gas.¹⁵¹ In a later study,¹⁵² polycrystalline copper films were obtained from Cu(acac)₂ vapour in pure hydrogen. The preparation of copper films with satisfactory characteristics from the same CCC but at higher substrate temperatures (*T_s*) of 300–450 °C (Table 3) has been patented.¹⁵³

A high temperature is required for CVD with Cu(acac)₂ as the starting compound. It was suggested that it may be decreased (by ~75 °) and the film deposition rate increased by using UV irradiation.¹⁵⁴

Yet another way for the activation of the CVD process involves the plasma-activated decomposition of Cu(acac)₂ vapour in hydrogen (PACVD), which allows generation of reactive hydrogen species at rather low temperatures.¹⁵⁵ For example, smooth thin copper films with a low SER (see Table 3) were obtained from Cu(acac)₂ vapour.¹³⁴ The decomposition was carried out in the presence of hydrogen (carrier gas) up to a substrate temperature of 300 °C; it was found that at higher temperatures decomposition does not depend on the nature of the carrier gas. This is apparently due to the fact that the amount of hydrogen formed upon intense pyrolysis in this temperature range is sufficient for the reduction of copper.¹⁴⁶ However, the presence of even small concentrations of O₂ results in an abrupt increase in the SER of the films.

If Cu(DPM)₂ vapour is used, the copper film growth on a quartz substrate starts at 350 °C.^{133, 156} The polycrystalline films obtained by this method¹³³ were preferentially oriented along the [111] direction and had a thickness > 300 nm and an SER of 10 μΩ cm (see Table 3). According to XPS data, carbon and oxygen were the main admixtures in this case (their total content was up to 10%); their simultaneous presence in the film could result from the reaction of copper with CO formed upon decomposition.¹⁴⁶

The specific electric resistance of copper films obtained¹¹⁶ from Cu(DPM)₂ vapour increased continuously from 8.1 to 41.2 μΩ cm (see Table 3) as their thickness decreased from 60 to 40.9 nm. It was noted that the films were smooth and mirror-like up to 300 °C but became dim as the temperature was increased. If the samples are cooled in a hydrogen atmosphere, carbon and oxygen admixtures in the film are virtually absent. On the other hand, cooling of the films in a nitrogen atmosphere results in a rather high content of the carbon admixture (12%–19%).

The factors determining the growth rate, the adhesion to the substrate and the morphology of the copper films obtained from Cu(DPM)₂ vapour in the CVD process were considered in detail by Dutta *et al.*¹⁵⁷ The effect of additional UV irradiation on such films was discussed:¹⁵⁰ at a constant substrate temperature, additional photostimulation of thermolysis decreased significantly the SER of the films (see Table 3).

The following variant of the CVD process has been suggested:¹⁵⁸ the vapour of the starting Cu(DPM)₂ was carried with a stream of nitrogen containing hydrogen and was then decomposed on a borosilicate glass substrate in the temperature range from 220 to 400 °C. In this case, the deposition of copper films was rather fast for Cu(DPM)₂ (26 nm min^{−1}) at a relatively low SER (1.7–2.7 μΩ cm at thicknesses ≥ 50 nm).

2. Polyfluorinated copper(II) β-diketonates

It is known that incorporation of fluorine atoms into molecules of organic compounds generally increases their volatilities, despite the essential increase in the molecular masses. The nature of this effect is still uncertain. It is assumed that it can be due to weakening of the van der Waals interactions^{111, 159} and (in some cases) due to the disappearance of hydrogen bonds upon replacement of hydrogen atoms in the molecule by fluorine atoms.¹⁰⁹ However, this can hardly be regarded as a comprehensive explanation.

Copper (II) β-diketonates also obey this rule.^{132, 159, 160} For example, replacement of methyl groups in the Cu(acac)₂ molecule by trifluoromethyl groups results in a 10⁴-fold increase in saturated vapour pressure of the chelate at constant temperature.¹⁶⁰ In addition, the thermal decomposition of polyfluorinated copper(II) β-diketonates results in films with a lower content of impurities (in particular, carbon). In most cases, the formation of copper fluorides is not observed even under rather drastic deposition conditions,¹⁶¹ though the formation of CuF as a labile intermediate product is possible. This can be due both to the relative strength of the C–F bond in comparison with the C–O and

Table 3. CVD conditions and properties of copper films obtained from copper(II) β-diketonates.

Starting MCC	<i>T</i> /°C	<i>T_s</i> /°C	Carrier gas	<i>P</i> /Torr	Substrate	SER /μΩ cm	Ref.
Cu(acac) ₂	—	220–250	H ₂ /Ar	—	SiO ₂ /Si	—	151
	—	220–250	H ₂	—	SiO ₂ /Si	1.7	152
	—	350–400	H ₂	—	SiO ₂ /Si	—	153
	110–170	< 300 ^a	H ₂	—	SiO ₂ /Si	1.8	134
Cu(DPM) ₂	110	350	H ₂	20	SiO ₂	10	133
	120	220–400	H ₂ /N ₂	5–10	SiO ₂ /Si	8.1–41.2	116
	—	250–350	H ₂	—	sapphire	4.6	150
	—	250–350 ^b	H ₂	—	"	1.7	150

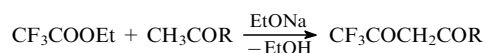
^a In plasma. ^b Under UV irradiation.

C—C bonds and to the high stabilities and volatilities of the polyfluorinated organic products of thermolysis. Owing to these properties, polyfluorinated copper(II) β -diketonates became the first CCC utilised in the CVD technology.¹¹⁰

Copper(II) hexafluoroacetylacetonate $\text{Cu}(\text{HFA})_2$ (**1**, $\text{R} = \text{R}' = \text{CF}_3$) is the polyfluorinated copper(II) β -diketonate studied most thoroughly and used most widely in the CVD process.¹¹¹ Copper(II) trifluoroacetylacetonate $\text{Cu}(\text{TFA})_2$ (**1**, $\text{R} = \text{CH}_3$, $\text{R}' = \text{CF}_3$) was also considered as a starting CCC. The use of copper(II) pivaloyltrifluoroacetylacetonate $\text{Cu}(\text{PTA})_2$ and some other substances of this series was much less common.

a. Synthesis and physicochemical properties

Polyfluorinated copper(II) β -diketonates are synthesised from the corresponding polyfluoro- β -diketones. These starting compounds were difficult to prepare¹⁶² until they became available by the Claisen condensation.^{163, 164}



$\text{R} = \text{CH}_3, \text{CF}_3, \text{etc.}$

This reaction became a reliable source of trifluoro- and hexafluoroacetylacetone and a series of their analogues.

The classical method for the synthesis of copper(II) hexafluoroacetylacetonate $\text{Cu}(\text{HFA})_2$ involves the reaction of copper(II) nitrate with hexafluoroacetylacetone in aqueous solution in the presence of sodium acetate (molar ratio 1:2:2).¹²⁰ This results in the precipitation of green crystals, the composition of which was determined differently by different researchers.^{119, 165, 166} It is believed¹²⁰ that these are the crystal hydrates $\text{Cu}(\text{HFA})_2 \cdot 2\text{H}_2\text{O}$ which do not decompose on sublimation. However, this conclusion was disputed later¹⁶⁷ and it was noted that the amount of water of crystallisation in the $\text{Cu}(\text{HFA})_2$ hydrate is not constant. According to the results of Funck and Ortolano,¹⁶⁷ the green crystals are monohydrates (see also Ref. 168), since the dihydrate isolated by them was a thermally unstable yellowish-green compound. Difficulties in assigning $\text{Cu}(\text{HFA})_2 \cdot n\text{H}_2\text{O}$ obtained by this method to mono- and dihydrates were also encountered later.¹⁶¹

Yet another method for the preparation of $\text{Cu}(\text{HFA})_2$ is the reaction of the ammonia complex of $\text{H}(\text{HFA})$ with CuCl_2 in aqueous solution.¹⁶⁹ The main product in the form of bluish-green crystals was characterised as a dihydrate, its melting point coincided with that reported previously.¹²⁰ Nevertheless, these data disagree with other reported results.¹⁶⁷

Yet another method for the synthesis of high-purity $\text{Cu}(\text{HFA})_2$ with the use of $\text{H}(\text{HFA})$ and copper(I) oxide was patented.¹⁷⁰

A drawback of the monohydrate $\text{Cu}(\text{HFA})_2 \cdot \text{H}_2\text{O}$ as the starting compound in the CVD processes is its ability to undergo decomposition with elimination of water in the reactor at low pressures in a carrier gas stream.¹⁷¹ Therefore, anhydrous $\text{Cu}(\text{HFA})_2$ is extensively used in these processes; under standard conditions, it has the form of purple crystals which are rather hygroscopic in air.¹²⁰

Copper(II) trifluoroacetylacetonate $\text{Cu}(\text{TFA})_2$ was first synthesised by Schultz and Larsen¹⁷² from the corresponding β -diketone (see also later studies^{164, 173}). A procedure for its preparation with the use of ammonium β -diketonate was reported.¹⁶⁹ Many fluorine-containing copper(II) β -diketonates [including $\text{Cu}(\text{TFA})_2$] and the corresponding β -diketones have been obtained by Park *et al.*¹⁷⁴

Generally, $\text{Cu}(\text{TFA})_2$ and $\text{Cu}(\text{HFA})_2$ are much more volatile than their analogues with alkyl groups described in the previous section.^{175–177} Furthermore, they were found to be the most volatile in a large series of fluorine-containing copper(II) β -diketonates, as indicated by thermogravimetric data.¹⁷⁸ The vapour pressure of $\text{Cu}(\text{HFA})_2$ measured by various methods^{179, 180} is 3 Torr at room temperature and atmospheric pressure.¹⁸¹

The initial study of the decomposition of $\text{Cu}(\text{TFA})_2$ and $\text{Cu}(\text{HFA})_2 \cdot \text{H}_2\text{O}$ vapour in the CVD process showed that the sublimation of these CCC occurs at 85 and 65 °C, respectively.¹¹⁰ The standard enthalpy of evaporation of $\text{Cu}(\text{HFA})_2$ is $13.2 \pm 0.8 \text{ kcal mol}^{-1}$ (see Ref. 180).

The β -diketonates of divalent copper containing the *n*-heptafluoropropyl group are rather exotic but quite suitable for the preparation of thin copper films by CVD. These compounds include such chelates as copper 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyloctane-3,5-dionate $\text{Cu}(\text{FOD})_2$ (**1**, $\text{R} = \text{Bu}^t$, $\text{R}' = n\text{-C}_3\text{F}_7$)¹⁸² and copper 1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluorononane-4,6-dionate $\text{Cu}(\text{FND})_2$ (**1**, $\text{R} = \text{R}' = n\text{-C}_3\text{F}_7$). These β -diketonates can be synthesised from β -diketones by the usual method.¹⁸³

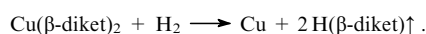
Stabnikov *et al.*¹⁸⁴ studied the possibility of synthesis of mixed-ligand copper(II) β -diketonates where the copper atom is simultaneously bound to diketones with alkyl (*acac*, *DPM*, *etc.*) and fluorinated alkyl groups (*TFA*, *HFA*). The crystal and molecular structures of some of these compounds were studied.^{160, 185–187} It was shown that they have intermediate properties between those of 'homogeneous' bisdiketonates incorporating the corresponding ligands; in the vapour phase, mixed-ligand compounds can undergo disproportionation to give homogeneous bisdiketonates. It was therefore concluded that these compounds have no advantages which would make them promising for practical use in CVD technologies.¹⁸⁴

b. Mechanisms of decomposition on the substrate surface

The thermal decomposition of $\text{Cu}(\text{HFA})_2$ vapour in CVD processes and its products have been studied in detail.^{139, 188, 189} It was shown that $\text{H}(\text{HFA})$ is the main decomposition product of $\text{Cu}(\text{HFA})_2$ in the vapour phase, while thermal decomposition on a SiO_2 surface at 480 °C can give either a CuO film (in air) or a film of metallic copper with small admixtures of Cu_2O and HFA decomposition products (in an argon atmosphere). The main decomposition product in air at 800 °C is Cu_2O in the form of finely dispersed particles.

As shown by Lecohier *et al.*,¹⁹⁰ the growth of a copper film from $\text{Cu}(\text{HFA})_2$ vapour involves several stages. During an induction period, the duration of which depends on the properties of the substrate surface and on the deposition method, film growth is not observed. Subsequently, the formation of isolated copper islets starts. Their merging results in a sharp decrease in the SER.

Van Hemert *et al.*¹¹⁰ suggested a mechanism of copper reduction from its chelate in a hydrogen atmosphere; this mechanism can be expressed by the overall equation



In the case of copper(II) β -diketonate hydrates, the formation of precursors in hydrated form was postulated.

A similar decomposition equation was suggested for the thermolysis of $\text{Cu}(\text{HFA})_2$ at relatively low temperatures (below 340 °C).¹⁸⁰

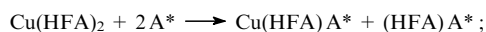
Thus, it is believed that thermolysis of the compounds in question starts with the cleavage of the copper—oxygen bonds. It was noted that at higher temperatures (500–600 °C) cleavage of the C—C bonds in the ligand also occurs and results in carbon admixtures in the film.

These concepts are basically correct but they do not provide a sufficiently full description of the processes occurring when the molecules of the starting CCC reach a heated substrate surface. A detailed scheme of these processes was developed somewhat later and generalised by Kim *et al.*¹⁹¹

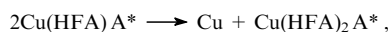
The following assumptions were used in the description of the mechanism of transformations in the CVD processes: the CCC and hydrogen molecules are adsorbed on different sites of the substrate surface; the adsorption of molecules of CCC competes with that of the original β -diketone formed upon reduction; the reduction occurs on the substrate rather than in the gas phase.

A scheme consisting of five basic steps was suggested based on these assumptions:

(1) adsorption of molecules of CCC with their partial dissociation

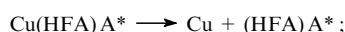


(2) disproportionation of partially adsorbed copper(I)-containing intermediates

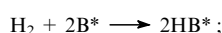


or

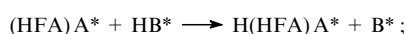
(2') progression of dissociation of the intermediate copper(I) derivative



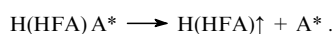
(3) dissociative adsorption of hydrogen



(4) formation of a volatile product, *viz.*, a β -diketone, on the surface



(5) desorption of the β -diketone



Here A^* and B^* indicate the active sites of, initially, the substrate and, later, the growing copper film capable of chemisorption.¹⁹² Step 4 is the limiting step of the entire process.^{192, 193}

A somewhat simplified version of this mechanism was suggested earlier.¹⁹⁴ It was noted that the irreversibility of the entire process begins in the step where metallic copper adsorbed on the substrate appears. The copper atoms form microclusters on the substrate surface, which consist of 8–12 copper atoms and are clearly separated from the organic ligands.¹⁹⁵

Certainly, the temperature of the process and the material of the substrate affect the course of the steps considered. A study of the thermodynamic parameters of the thermal decomposition of Cu(HFA)_2 and the phase compositions of the copper films formed in a rather broad temperature range showed that copper(I) fluoride can be formed in one of the intermediate steps at rather low temperatures. This is not taken into account in the scheme suggested above. As the temperature increases, the amount of CuF decreases until it disappears completely.¹⁹⁶

The effect of the substrate material on the mechanism of thermolysis of Cu(HFA)_2 vapour was analysed in detail.¹⁹⁷ It was noted that decomposition of Cu(HFA)_2 in a stream of H_2 on a TiN surface can result in replacement of fluorine atoms in the trifluoromethyl group by hydrogen atoms. In the case of the SiO_2 substrate, a noticeable amount of CF_3COOH is formed, which is the product of cleavage of the $\text{C}-\text{C}$ bonds in the HFA fragment.

Let us outline the applicability limits of the mechanism considered. Two types of CVD processes are distinguished, depending on the conditions.¹⁹⁸ At rather low temperatures and partial vapour pressures of the starting CCC, the process is primarily characterised by reactions on the substrate surface occurring in accordance with the mechanism described above (the so-called reaction-limited conditions). At high substrate temperatures and pressures in the reactor and at high vapour pressures of the substance, this mechanism does not operate and the film deposition process is characterised by the transport of molecules of CCC to the substrate (transport-limited conditions). These conditions generally result in film heterogeneity.¹⁹⁸

In order to reveal the details of the thermal decomposition mechanism of Cu(HFA)_2 on various substrates, some authors used ultrahigh vacuum conditions ($\leq 10^{-7}$ Torr). Such conditions are unlikely to be suitable for industrial CVD processes, but we feel that the results obtained should be discussed.

If thermal decomposition of Cu(HFA)_2 vapour during CVD is carried out in ultrahigh vacuum, the process mechanism changes

essentially. In this case, disproportionation of the intermediate copper(I) derivative does not occur.¹⁹⁹ For example, the Cu(HFA)_2 molecules are quickly desorbed from the TiN substrate at as low temperature as 75 °C, and further decomposition of the intermediate [reaction (2'), see above] becomes the dominating process. At 200 °C, decomposition of the adsorbed ligand begins to give CO, CO_2 and CF_4 ; as a result, $\sim 30\%$ of Cu from the starting material remains on the substrate.

Disproportionation of copper(I) intermediates is not observed, either, in the deposition of copper films onto polycrystalline tantalum substrates from Cu(HFA)_2 vapour.²⁰⁰ It was noted that adsorption of CCC on a tantalum surface starts at 158 °C; formation of a copper film occurs at temperatures ≤ 117 °C, while diffusion of copper into tantalum is observed at 477 °C.

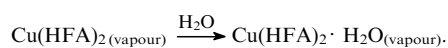
The adsorption of Cu(HFA)_2 molecules and their subsequent decomposition on the (100) and (111) surfaces of copper single crystals in ultrahigh vacuum (10^{-10} Torr) have been studied.²⁰¹ It was shown that under these conditions, surface migration of ligands of the adsorbed molecules of CCC with formation of isolated HFA groups adsorbed on the substrate parallel to its surface occurs even at low temperatures (~ -73 °C). At 102 °C, their decomposition gives CO, CO_2 (quickly desorbed from the substrate), CF_3 and the ketenylidene fragments $\text{C}=\text{C}=\text{O}$ adsorbed through the terminal carbon atom. At temperatures above 227 °C, the CF_3 species are desorbed, while the $\text{C}=\text{C}=\text{O}$ fragments undergo decarbonylation; the carbon remaining on the surface is the basic source of film contamination.

As shown for the adsorption of Cu(HFA)_2 on a platinum surface under similar conditions,²⁰² the orientation of HFA groups depends on the thickness of the layer of molecules of CCC adsorbed on the substrate. Ligand orientation parallel to the substrate surface is characteristic of very thin films; as their thickness increases, the ligands are 'reoriented' to become perpendicular to the substrate. It was also noted that difluorocarbene CF_2 is the most strongly adsorbed species, which is desorbed in ultrahigh vacuum only at 577 °C.

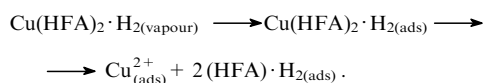
The nature of interaction of Cu(HFA)_2 and the β -diketone H(HFA) itself with the surface of the SiO_2 substrate was studied in detail.²⁰³ The experiments were carried out in ultrahigh vacuum (5×10^{-8} Torr). In this case, everything is determined by the presence of OH groups, both isolated and connected by hydrogen bonds, and siloxane bonds, $\text{Si}-\text{O}-\text{Si}$, on the surface of the substrate. It was shown that preferential adsorption of Cu(HFA)_2 molecules at 25 °C occurs with involvement of isolated surface OH groups. On heating the substrate (studied in the range up to 400 °C), decomposition of adsorbed Cu(HFA)_2 was observed; in this case, the OH groups involved in the adsorption were not recovered.

Farkas *et al.*²⁰³ reported experiments aimed at decreasing the density of OH groups on a SiO_2 surface as a result of its thermal treatment. It was found that in this case strong adsorption of the Cu(HFA)_2 molecules involves surface siloxane bonds, which are cleaved irreversibly upon subsequent heating and thermolysis of Cu(HFA)_2 . However, desorption of the decomposition products occurs at rather high temperatures, *viz.*, about 400 °C irrespective of pretreatment of the SiO_2 surface. The mechanism suggested by the authors involves direct axial coordination of the copper(II) atom with the non-shared electron pairs of the oxygen atoms of the OH groups or the $\text{Si}-\text{O}-\text{Si}$ bonds, giving a five-coordinate complex. A similar explanation was suggested previously for the interaction of Cu(acac)_2 with a SiO_2 surface.²⁰⁴

The deposition mechanism of copper films from Cu(HFA)_2 vapour in the presence of water vapour was considered in detail.^{205–208} It was assumed that intermediate formation of a Cu(HFA)_2 mono- or dihydrate occurs in the gas phase

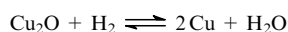


In the resulting complex (under gas-phase conditions) an intramolecular transfer of H₂O protons to the ligand occurs, which weakens the copper–oxygen bonds. Adsorption of this complex on the surface results in elimination of the hydrated enol form of the β -diketone



The adsorbed Cu²⁺ ions are reduced under the action of hydrogen.

Since reduction is the limiting step of the process, the side formation of copper(I) oxide is observed at low deposition temperatures.^{209,210} It was found with the use of the ¹⁸O isotope that the formation of an oxide phase involves the oxygen atoms of H₂O rather than those of the H(HFA) ligand.²⁰⁹ However, in general, the addition of water vapour to the carrier gas in an optimum temperature mode does not result in contamination of films with copper oxides. This is believed to be due to the fact that the reduction of copper



is an exothermic process (the equilibrium constant is 0.78×10^8 at 325 °C).²⁰⁵

The presence of water vapour in the carrier gas improves the morphological characteristics of the films. This can be due to the fact that the nucleation rate of copper is determined by the rather low activation energy for decomposition of the adsorbed Cu(HFA)₂ hydrate and hence almost does not depend on the properties of the substrate surface. Owing to the high density of the nucleation centres determined by the amount of the adsorbed hydrate, smooth films with good morphology are formed. On the other hand, the formation of film nuclei in usual systems is limited by a surface reaction between the adsorbed molecules of anhydrous CCC and hydrogen, the rate of which depends on the density of the adsorption centres on the substrate surface. In this case, the film is very sensitive to the quality of the substrate.²⁰⁵

The role of molecules of an alcohol in the deposition of copper films from vapour of solutions of the starting CCC in the alcohol is somewhat similar to the role of water molecules.

Like water, methanol and ethanol in the vapour phase can be coordinated with the copper(II) ion in copper β -diketonate; as a result, molecules of the complex of copper β -diketonate with the corresponding alcohol are deposited on the substrate.²⁰⁸ The proton of the alcohol molecule in the adsorbed complex can then be transferred to the adsorbed HFA ligand obtained due to the CCC decomposition; this favours the desorption of an H(HFA) molecule from the substrate surface. An adsorbed alkoxy group that remains on the surface can be removed by two pathways: either by elimination of the hydrogen atom from the α -carbon atom to give a volatile carbonyl compound, or by the reaction with the adsorbed hydrogen atom from the carrier gas to give the alcohol.^{211,212} In the former case, the alcohol acts as a reducing agent, while in the latter case, as a reduction catalyst. Propan-2-ol is the most efficient compound,²¹³ in spite of the fact that propan-2-olic complexes of copper β -diketonates are the least stable complexes with alcohols.²⁰⁸

The mechanism of photochemical deposition of copper films from the vapour of CCC under laser irradiation of substrates was suggested and considered in detail by Ehrlich and Tsao.²¹⁴ Special attention was given to film growth rate simulation.

A study by Zheng *et al.*²¹⁵ dealt with the mechanism of Cu(HFA)₂ vapour decomposition in a stream of hydrogen under exposure to plasma. It was shown that under these conditions preferential consecutive elimination of CF₃ groups from the ligand is observed, rather than elimination of the entire ligand with cleavage of the Cu–O bonds. Nevertheless, this decomposition pathway also gives only volatile organic products which do not contaminate the film obtained.

The thermodynamics of decomposition of Cu(HFA)₂ and its analogue, Cu(FOD)₂, in the PACVD process has been considered.²¹⁶

The authors of the first studies on the PACVD method for the preparation of copper films assumed that the role of plasma involves the formation of a high concentration of reactive hydrogen species.^{155,216,217} However, the details of the mechanism remained unclear. A model of decomposition of Cu(HFA)₂ with the use of hydrogen plasma was described.¹⁹³ It was noted that in this process the hydrogen plasma is mainly electropositive and consists of cations, *i.e.*, H⁺, H₂⁺ and H₃⁺, electrons and hydrogen atoms. The overall process occurs according to the five-step mechanism discussed above; however, both the hydrogen atoms adsorbed on the substrate and the hydrogen atoms from the gas phase can participate in the limiting fourth step. The film quality and the deposition rate are determined by the pressure in the reactor, the electric field power and the substrate temperature. At small power (up to 25 W), the following kinetic equation is valid:

$$R_d = k[\text{Cu(HFA)}_2]^{1/2}[\text{H}] ,$$

where R_d is the rate of the direct deposition reaction, k is the rate constant of the limiting (fourth) step. At high electric field power, decomposition of HFA fragments starts, the process becomes more complicated and strong contamination of films with carbon and fluorine is observed.¹⁹³

The decomposition mechanisms of other fluorinated copper(II) β -diketonates in CVD processes have almost not been studied. It was shown¹⁸⁹ that H(FOD) is the main product of Cu(FOD)₂ decomposition in the vapour phase. One can also mention a study of the kinetics of thermal decomposition of Cu(PTA)₂ vapour upon heating of the substrate with a CO₂ laser;²¹⁸ the observed phenomena are in full agreement with the concepts of the reaction-limited and transport-limited processes as a function of deposition conditions. Data are available on the products of Cu(FND)₂ thermolysis and its behaviour under CVD conditions in the presence of vapour of water and alcohols.²⁰⁸

c. Preparation and characteristics of copper films

In the first experiments on the preparation of thin copper films by CVD based on decomposition of Cu(TFA)₂ and Cu(HFA)₂ · H₂O vapour in a stream of hydrogen under atmospheric pressure, the optimum temperature of glass substrates on which films are formed was found to be 250 °C. However, the characteristics of films were not reported.¹¹⁰ The decomposition was purely thermal, without additional activation with laser radiation or plasma. A little later, a similar procedure was patented by the same authors.²¹⁹

The process of non-activated thermal deposition of copper films from Cu(HFA)₂ vapour was also studied in a number of works (see, *e.g.*, Refs 40, 115, 180, 191, 194, 219–244).

Typical conditions were used by Kim *et al.*:¹⁹¹ the pressure in the reactor was 10 Torr, the temperature of the TiSi₂/Si substrate was 300–400 °C, an H₂/Ar mixture (3 : 1) was used as the carrier gas (Table 4). It was found that at low pressure and with this substrate material, no growth of the copper film on the substrate occurred at temperatures up to 300 °C. Above this temperature, the growth rate was 10–100 nm min^{−1}. The film thickness depended linearly on the deposition rate, *i.e.*, the deposition rate was practically the same in each experiment. As the hydrogen partial pressure in the carrier gas was decreased, a considerable decrease in the deposition rate was observed. The surface morphology of the films obtained under these conditions was studied in detail.^{220,223}

The deposition of copper films by decomposition of Cu(HFA)₂ vapour on SiO₂/Si substrates in the temperature range from 250 to 650 °C in the absence of hydrogen (with pure argon as the carrier gas) was studied by Temple *et al.*,¹⁸⁰ who did not observe the formation of films at 250 °C, as opposed to the results of other studies.¹¹⁰ Pure copper films appeared in the

Table 4. CVD conditions and properties of copper films obtained from polyfluorinated copper(II) β -diketonates.

$T / ^\circ\text{C}$	$T_s / ^\circ\text{C}$	Carrier gas	P /Torr	Substrate	SER / $\mu\Omega$ cm	Ref.
Starting CCC — Cu(HFA) ₂						
—	300–400	Ar/H ₂	10	TiSi ₂ /Si	2.0	191
—	300–400	Ar	10	TiN/Si TiW/Si	2.0	221, 222
—	—	—	—	Cr (on Si)	1.7	224
97–120	340–390	Ar	8–10	SiO ₂ /Si	3–7	180
—	250–300	H ₂ /Ar	0.75	Si, SiO ₂	1.9	115
—	250	H ₂ /He	2–10	glass	2–3	194
80–100	160–170 ^a	H ₂	1–1.7	Si, Ti, W	1.7–1.9	244
65–85	310–390	H ₂	15	Au/Si	2.5 $\pm$ 0.3	218
65–90	310–390	H ₂ /Ar	2–20	SiO ₂ , TiSi ₂	2.0 $\pm$ 0.1	220
60	300–400	H ₂	0.15	SiO ₂ /Si	—	199
—	800 ^b	—	—	—	3.6 $\pm$ 0.1	236
60	400 ^c	He/H ₂ O	0.075	SiO ₂ /Si	2	190
75–94	350–410	H ₂ /H ₂ O	15	Ta/SiO ₂	2.0	205
65–85	310–390	H ₂ /Ar	2–10	SiO ₂ /Si, TiSi ₂	2.0–2.3	223
100	130–200 ^c	H ₂ /Ar	760	SiO ₂ /Si	—	241
95–98	300	H ₂	1–10	TiN/Si	2.5–5	211
—	230 ^a	H ₂	2	SiO ₂ , Si, Al	2.0	243
—	160–170 ^a	H ₂	—	SiO ₂ /Si W/Si	1.7–1.9	244
80	225 ^a	H ₂ /Ar	1	Si	1.7	215
Starting CCC — Cu(FOD) ₂						
—	< 250	H ₂	1–10	SiO ₂ , Si, Al	3.0	182
—	300–400	H ₂	1–10	SiO ₂ , Si, Al	1.8	182

^a In plasma. ^b Under laser irradiation followed by cooling to 250 $^\circ\text{C}$. ^c Under laser irradiation.

temperature range of 340–390 $^\circ\text{C}$ (see Table 4). Upon further heating of the substrate to 430 $^\circ\text{C}$, the films containing 65% of carbon (25% of copper) were formed, while the films obtained at 500 $^\circ\text{C}$ consisted of pure carbon.

In other studies, the temperature range for the formation of pure copper films by decomposition of Cu(HFA)₂ vapour in argon was somewhat wider, *viz.*, from 310 to 400 $^\circ\text{C}$.^{221, 222} Films of rather high quality were obtained with a growth rate of 65 nm min^{−1}. It was noted that the substrate (TiN, TiW) surfaces had to be cleaned from oxide contaminants.²²²

Awaya and Arita²²⁴ synthesised copper films from Cu(HFA)₂ vapour on a Si substrate coated with a few buffer layers at once (the top layer consisted of chromium, see Table 4). Such films had low SER values and contained an admixture with chromium.

In addition to hydrogen, water can be used as a reducing agent for Cu(HFA)₂.^{171, 190, 205, 225, 226} In this case, the growth rate of copper films depends directly on the amount of water vapour in the gas phase.²²⁵ The presence of water vapour during the decomposition of Cu(HFA)₂ vapour increases considerably the film growth rate (approximately by two orders of magnitude¹⁷¹) but the selectivity of the process decreases (see Section VI). The specifics of the film growth kinetics in this method and the film morphology were considered in detail.¹⁹⁰ It was reported¹⁷¹ that the SER of the resulting films can be as low as ~ 2.0 – $2.1 \mu\Omega$ cm while the deposition rate remains high.

Another group of researchers who studied a similar process suggested the use of Cu(HFA)₂ dihydrate rather than Cu(HFA)₂ as the starting CCC.²⁰⁵ They reported a high deposition rate and good morphology of the copper film surfaces. However, the results of this study were poorly reproducible, probably due to the instability of the dihydrate; it was reported that this substance readily eliminates water molecules in the vapour phase.²²⁷ The use of anhydrous Cu(HFA)₂ in the presence of water vapour gave films with low SER (deposition rates up to 90 nm min^{−1}).

An interesting modification of the method considered above involves the deposition of copper films from the vapour phase of a CCC solution in an alcohol.²¹¹ It is known that anhydrous Cu(HFA)₂ is freely soluble in alcohols (ethanol, propan-2-ol). In

this method, a stream of the carrier gas (H₂) is passed through an $\sim 0.4 \text{ g ml}^{-1}$ alcoholic solution of Cu(HFA)₂ (higher concentrations result in an increased solution viscosity and, as a consequence, instability of the process). The alcohol vapour present in the gas phase serves as an additional reducing agent.

The advantage of this technique is the significant (approximately fivefold²¹¹) increase in the deposition rate of copper films in comparison with that in the usual process in a stream of hydrogen. However, the films obtained using this technique have higher porosity which inevitably impairs their properties. For example, the SER of copper films synthesised by Borgharkar *et al.*²¹¹ was 2.5–5 $\mu\Omega$ cm (see Table 4) provided that their thickness was no less than 1000 nm. The characteristics of these films can be improved by addition of water vapour to the carrier gas; in this case, the SER of the films was 2.6–2.9 $\mu\Omega$ cm.²¹¹ A technique for CVD of copper films from CCC with participation of a solvent has been patented.²²⁸

Attempts at performing the CVD process with Cu(HFA)₂ with an excess of the starting β -diketone H(HFA), which in turn is a decomposition product of the precursor, were reported. It was noted¹⁹⁴ that the excess of H(HFA) decreased the copper film deposition rate. Nevertheless, if SiO₂ templates deposited on a copper substrate were used for the preparation of thin copper strips from Cu(HFA)₂, pretreatment of the template channels with H(HFA) vapour improved considerably the characteristics of the strips, but the presence of H(HFA) vapour during the deposition process is unacceptable as it caused an abrupt impairment of the strip morphology and a loss of selectivity.²²⁹

It is known that polyfluorinated copper(II) β -diketonates are photo-labile compounds. Their photochemistry in solution²³⁰ and in the gas phase^{231–233} has been studied rather thoroughly. Laser irradiation of the substrate is a popular method for decomposition of the vapour of these compounds for deposition on substrates.^{181, 232, 234–238} In this case, Cu(HFA)₂ itself or its alcoholic solution (an ‘alcoholic’ CVD technique) can be utilised for the preparation of films.

This creates certain difficulties. First, it is difficult to estimate to what degree the observed process is pyrolytic and to what

degree it is photochemical, as the substrate temperature is $\sim 250^\circ\text{C}$,²³⁶ and it is difficult to estimate accurately the temperature of the process in laser experiments.²³⁹ It is known that the quantum yield of decomposition of copper(II) β -diketonate vapour to the metal is rather small; this determines the low film growth rates by the purely photochemical mechanism and the irregularity of their morphology. Second, photochemical decomposition can increase the content of the carbon admixture in the copper film; fluorine and oxygen are removed with the volatile photolysis products.²³⁴ It was shown in experiments on copper film deposition under laser irradiation with a wavelength corresponding to the visible spectrum range that carbon is a photolytic admixture in this case; under these conditions, the carbon contamination of the films was absent.²³⁶

A thorough refinement of the photochemical process modes for the deposition of films was required to overcome the difficulties noted above.^{237, 240} In a study devoted to the effect of laser power on the growth rate of copper films from $\text{Cu}(\text{HFA})_2$ vapour,²⁴¹ the deposition rate was increased from 20 to 120 nm min^{-1} in a stream of an argon–hydrogen mixture and from 4 to 27 nm min^{-1} in a stream of argon, but the SER of the films were not reported. It was noted that in the presence of ethanol under laser activation conditions, as in the usual thermolysis, the growth rate of copper films increased.^{234, 238}

The properties of films obtained with the use of a laser were analysed by Hoyle *et al.*²³⁶ The films were formed on a silicon substrate at $\sim 800^\circ\text{C}$ (the power density of laser radiation was $4 \times 10^5 \text{ W cm}^{-2}$). As the film grew, the substrate temperature decreased gradually to 250°C , *i.e.*, the optimum value for $\text{Cu}(\text{HFA})_2$ vapour decomposition. The films had good adhesion properties but rather high SER values (see Table 4).

The preparation of film microstructures (copper microstrips) from $\text{Cu}(\text{HFA})_2$ vapour is a promising field of application of the CVD process with the use of laser radiation. The optimum conditions of the process for the preparation of strips 2 mm long were chosen and the factors determining their basic characteristics were studied.²⁴⁰

A milder way of photochemical decomposition of $\text{Cu}(\text{HFA})_2$ vapour is the use of UV irradiation.²⁴² In this case, the level of contamination of copper films is much lower.

Yet another method for activation of decomposition of $\text{Cu}(\text{HFA})_2$ vapour is the use of plasma.^{161, 243, 244} It was shown in the very first study on this technique that if the process is carried out in a stream of hydrogen, high-quality thin copper films could be obtained virtually without carbon admixtures by varying the source power and the substrate temperature.¹⁶¹ The SER of the best film samples, 60–80 nm thick, were within 1.7–2.4 $\mu\Omega \text{ cm}$; these values could not be reached with laser radiation. This can be due to the fact that efficient growth of films in the plasma method requires a considerably lower source power; an increase in the power immediately resulted in carbon contamination.

Plasma activation was used to improve considerably the characteristics of the copper films obtained by the 'alcoholic' method. For example, decomposition of the vapour of an ethanolic solution of $\text{Cu}(\text{HFA})_2$ in a stream of hydrogen at a plasma source power of 45 W gave a copper film 63 nm thick with a low SER (see Table 4).²⁴³ An optimum content of hydrogen in the carrier gas is a prerequisite for the preparation of high-quality copper films by this method: at a hydrogen concentration lower than 88%, the SER of copper films increased to 9–10 $\mu\Omega \text{ cm}$. An opposite relationship was observed for the grain size in the copper film: a decrease in the fraction of hydrogen in the carrier gas decreased the grain size from ~ 100 (88% H_2) to ~ 10 nm (0% H_2). The reasons for this phenomenon were not rationalised.

Copper films with good characteristics were obtained²⁴⁴ using a similar technique by decomposition of the vapour of $\text{Cu}(\text{HFA})_2$ solutions in ethanol and propan-2-ol at relatively low substrate temperatures and a power density of the plasma source of 0.13–0.25 W cm^{-2} . A high film growth rate, *viz.*, 25 nm min^{-1} , was reported; the SER of films 440 nm thick was 1.7–1.9 $\mu\Omega \text{ cm}$.

Polycrystalline copper films 500–1000 nm thick were obtained from the vapour of a rather rare starting CCC, *viz.*, $\text{Cu}(\text{FOD})_2$.¹⁸² The resulting copper film (argon as the carrier gas) contained up to 24% admixtures (C, O, F). Replacement of argon with hydrogen resulted in a pure copper film with good characteristics; in this case, a decrease in the substrate temperature (to 250°C and lower) increased the SER of the films considerably (see Table 4).

3. Complexes of copper(II) β -diketonates with additional ligands

The copper atom in copper(II) β -diketonates is coordination-unsaturated, hence it is possible to synthesise adducts of copper(II) β -diketonates with various organic Lewis bases (primarily, nitrogen- and oxygen-containing ones). Some of these adducts are volatile. However, the prospects of their use in the CVD technology as precursors are doubtful.

Unlike copper(I) β -diketonates, copper(II) β -diketonates are convenient starting CCC for the CVD technology. As a rule, it is easier to change their properties by modifying the starting β -diketone than to try to obtain a stable adduct with an additional ligand which can be sublimed.

Nevertheless, the use was suggested of some compounds of this type as volatile CCC, for example, the adduct of $\text{Cu}(\text{DPM})_2$ with *o*-phenanthroline (1 : 1), which is sublimed *in vacuo* at 130°C without decomposition.²⁴⁵ Under the same conditions, $\text{Cu}(\text{DPM})_2$ itself is sublimed at 160°C . It was reported that an attempt at sublimation of a similar $\text{Cu}(\text{acac})_2$ adduct resulted in its decomposition.

The 1 : 1 adducts of $\text{Cu}(\text{HFA})_2$ and $\text{Cu}(\text{PTA})_2$ with *o*-phenanthroline and 2,2'-bipyridyl are also volatile.²⁴⁶ However, the sublimation temperatures for all four adducts exceed 160°C , which is higher than those for the original copper β -diketonates.

More promising in this respect is the synthesis of a series of volatile adducts of $\text{Cu}(\text{HFA})_2$ with ethanolamines.²⁴⁷ As noted above, the addition of ethanol vapour to the carrier gas increased the copper film deposition rate. It was assumed that the ethanol-amine adducts obtained, which contained a 'preformed' ethanol fragment, will maintain this advantage; on the other hand, the presence of the amino group should impart stability to the adduct under sublimation conditions.

Preliminary CVD experiments on this type of copper(II) derivatives showed that the adduct of $\text{Cu}(\text{HFA})_2$ with 1-dimethylaminopropan-2-ol, which forms a copper film at a substrate temperature of 300°C , has quite satisfactory characteristics suitable for CVD processes.²⁴⁷ However, the parameters of the process and the film characteristics were not reported. No films were obtained with the use of a similar adduct with ethanolamine.

4. Other classes of volatile compounds of copper(II)

The range of volatile organic derivatives of copper(II) suitable for CVD processes is not limited to β -diketonates, but the choice is rather narrow.

a. Chelate complexes, analogues of copper(II) β -diketonates

Nitrogen-containing analogues of β -diketones (iminoketones) form volatile derivatives of copper(II) with physicochemical properties satisfactory for CVD processes.²⁴⁸ Nevertheless, we could find only one study devoted to the practical preparation of copper films from this class of compound.²⁴⁹ A new compound synthesised by the authors, *viz.*, bis[4-(2,2,2-trifluoroethyl)imino-1,1,1,5,5,5-hexafluoropentan-2-onato]copper(II) designated as $\text{Cu}(\text{nona-F})_2$, had a decomposition temperature of 270°C . Copper films with satisfactory characteristics were obtained from this compound but no further developments were reported.

Of compounds the structure of which is somewhat similar to that of copper β -diketonates, chelate complexes of copper(II) with analogues of ethyl acetoacetate ($\text{CH}_3\text{COCH}_2\text{COOR}$) can be considered as a real alternative to the former. A series of these compounds ($\text{R} = \text{Me}, \text{Et}, \text{Bu}^t, \text{CH}_2\text{Ph}$ and $\text{CH}_2\text{CH}_2\text{OCH}_3$), their hydrates and adducts with alcohols were synthesised²⁵⁰ using a

technique similar to that used for copper β -diketonates.¹²⁰ The sublimation temperatures of these compounds were from 78 to 113 °C at 0.16 Torr. The crystal structure of $\text{Cu}(\text{CH}_3\text{COCHCOOBu}^t)_2$ monohydrate was determined.¹³⁶

CVD experiments with compounds of this series at low pressures (0.1–1 Torr) in the presence of hydrogen resulted in high-quality copper films with SER values ranging from 1.8 to 2.5 $\mu\Omega$ cm; in addition, the factors determining their adhesion to the substrate were studied.^{250, 251} A Si substrate with a TiN or TiW barrier layer was used; the deposition rate varied from 0.5 to 20 nm min⁻¹ at substrate temperatures from 160 to 330 °C. Judging by the characteristics of the films obtained, $\text{Cu}(\text{CH}_3\text{COCHCOOCH}_2\text{CH}_2\text{OCH}_3)_2$ was the best starting CCC in this series.²⁵⁰

If copper(II) ester chelates are used, copper films are formed at a relatively low substrate temperature (160 °C). For comparison: the minimum substrate temperature is 310 °C for $\text{Cu}(\text{HFA})_2$.^{220, 223} This is an important advantage of copper(II) ester chelates in comparison with copper(II) β -diketonates. No noticeable thermolysis of the adsorbed free ligands occurs at 160 °C; this ensures that the films are not contaminated.

The surface morphology of copper films synthesised by the CVD method from $\text{Cu}(\text{CH}_3\text{COCHCOOBu}^t)_2$ vapour was studied in detail.²⁵² Comparison of the deposition processes and microstructures of copper films obtained from $\text{Cu}(\text{DPM})_2$ and $\text{Cu}(\text{CH}_3\text{COCHCOOBu}^t)_2$ showed that dense, crack-free films are formed from both CCC at substrate temperatures up to 350 °C, but the substrate temperature required for the deposition is about 100 °C lower in the case of $\text{Cu}(\text{CH}_3\text{COCHCOOBu}^t)_2$.^{253, 254} The growth rate of the copper film from $\text{Cu}(\text{CH}_3\text{COCHCOOBu}^t)_2$ vapour is several-fold smaller, but the film structure is much better than that of the film obtained from $\text{Cu}(\text{DPM})_2$ vapour. In another study by the same scientific group,¹¹⁷ the SER of copper films synthesised from $\text{Cu}(\text{CH}_3\text{COCHCOOBu}^t)_2$ at 225 °C was reported to be 2.5–4.0 $\mu\Omega$ cm at a film thickness of 50–120 nm.

$\text{Cu}(\text{CH}_3\text{COCHCOOEt})_2$ is also believed by many authors to be a promising starting CCC for the deposition of copper films. For example, dense fine-grain copper films ≥ 95 nm thick were obtained from this compound at 225 °C (on a SiO_2 substrate) in a hydrogen atmosphere;²⁵⁵ the SER of these films was close to that of metallic copper. This compound was also used²⁵⁶ in a CVD process with plasma activation giving a copper film > 250 nm thick with a SER of 2.0 $\mu\Omega$ cm. The same work also reported the preparation of a 256 Mb RAM chip by CVD using decomposition of $\text{Cu}(\text{CH}_3\text{COCHCOOEt})_2$ vapour.

b. Copper(II) carboxylates

Copper(II) carboxylates that are more readily accessible synthetically than copper β -diketonates could become a real alternative to the latter in CVD processes. However, the use of this class of substances, first of all copper(II) formate $\text{Cu}(\text{HCOO})_2$, for the preparation of copper films was originally limited to deposition from liquids and aerosols.^{63, 257, 258}

Nevertheless, it was shown subsequently that $\text{Cu}(\text{HCOO})_2$ hydrate can be directly used in the CVD process.^{259, 260} Preparation of copper films from the vapour of this compound was carried out on Si(100) and TiN substrates at 200–350 °C with and without a carrier gas (H_2 , Ar). The highest-quality crystalline copper films without oxygen admixtures were obtained at a substrate temperature of ~ 300 °C.

Of copper carboxylates intended as potential starting CCC, volatile complexes of copper(II) polyfluorocarboxylates with 1,4-dioxane were also obtained; these compounds can sublime without decomposition at 120–130 °C (0.05 Torr).²⁶¹

c. Copper(II) alkoxides and their derivatives

Volatile alkyl derivatives of copper^{262, 263} cannot be regarded as technologically suitable compounds, both with respect to their

synthetic accessibility and properties. Alkoxide derivatives of divalent copper are much more stable and accessible.

The simplest copper(II) alkoxides of the type $\text{Cu}(\text{OR})_2$, where $\text{R} = \text{Me}$, Et, etc., are unsuitable for CVD processes because they are polymeric non-volatile compounds.²⁶⁴ Compounds obtained by partial replacement of hydrogen atoms in Cu(II) alkoxides by fluorine atoms sublime at 80–90 °C. Their thermal decomposition occurs at 140–200 °C,²⁶⁵ but these compounds have not been studied from the viewpoint of their use in CVD technology. Attempts were made to synthesise monomeric alkoxides as the starting compounds for CVD processes.^{266, 267} In fact, a series of convenient compounds [e.g., $\text{Cu}(\text{OCH}_2\text{CH}_2\text{NR}_2)_2$, where $\text{R} = \text{Me}$, Et] which sublime *in vacuo* at 60–110 °C were obtained, but no experiments on the preparation of copper films using CVD from them as the starting CCC were carried out.

An interesting development of this line of research was a rather simple synthesis of volatile complexes of copper(II) fluoroalkoxides with various nitrogen-containing Lewis bases with general formula $\text{Cu}(\text{OR})_2 \cdot \text{L}$, where R is hexafluoroisopropyl $\text{CH}(\text{CF}_3)_2$ (HFIP) and $\text{C}(\text{CH}_3)(\text{CF}_3)_2$, while $\text{L} = \text{N}, \text{N}', \text{N}'', \text{N}'''$ -tetramethylenediamine (TMED) and 2,2'-bipyridyl.²⁶⁸ These complexes are monomeric and undergo sublimation with partial decomposition. However, it was shown that decomposition of vaporised $(\text{HFIP})_2\text{Cu}(\text{TMED})$ complex on silicon substrates at 300 °C gives a copper film with an admixture of < 1% carbon. However, in the authors' opinion,²⁶⁸ the search for starting compounds which would be more competitive with copper β -diketonates among this class of compounds is necessary.

V. The starting copper-containing compounds: copper(I) derivatives

Disproportionation to copper(II) derivatives and metallic copper is one of the main reactions of copper(I) compounds. It is no wonder that this process attracted the attention of researchers in the field of preparation of thin copper films by the CVD process.

It is known that it is more difficult to synthesise volatile copper(I) derivatives than similar compounds containing copper(II). However, studies in the field of CVD processes with the use of monovalent copper compounds, which have started rather recently, are very intense.^{111, 269} This is due to the fact that thermally induced disproportionation has certain advantages over thermal decomposition.

These advantages include the following: the process occurs with higher deposition rate and at lower temperatures; the ligands bound to the Cu(I) atoms are removed in a more favourable temperature range without decomposition to volatile products. This provides good technological characteristics: the process is safer as generally there is no need to use a carrier gas and hydrogen as the reducing agent; a high-purity film grows because it is not contaminated with carbon, fluorine and oxygen. These advantages expand the prospects and reduce the restrictions related to the design and control of the technological process of selective deposition of copper films.

It should be noted that in the case of CVD processes involving copper(I) derivatives, a certain competition exists between the CCC with organic ligands and the starting inorganic CCC (usually, copper halides).

Attempts were made to use copper(I) halides for the preparation of copper films by the CVD method.^{270, 271} High evaporator temperatures are required in this case; in addition, the problem of film purity arises owing to the low volatility of the starting compounds.¹¹¹ Copper(I) halides are more volatile than copper(II) halides.^{272–274} For example, dense fine-grain copper films with SER of 1.9 $\mu\Omega$ cm devoid of iodine admixture were obtained from CuI (the temperature of the SiO_2 substrate was 697 °C).²⁷⁴ However, too high substrate temperatures are required for CVD process based on monovalent copper halides; this limits essentially the use of these compounds.

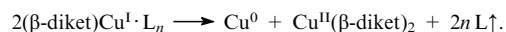
1. Copper(I) β -diketonates and their complexes

Among volatile copper(I) compounds, as among copper(II) derivatives, β -diketonates are promising for CVD technology. These compounds are attractive due to their ability to undergo disproportionation at comparatively low temperatures to give the corresponding volatile copper(II) β -diketonates and metallic copper directly in the form of thin films



However, the operation with copper(I) β -diketonates has specific difficulties. First, the contact of these compounds with atmospheric oxygen during synthesis results in their smooth oxidation to the corresponding copper(II) β -diketonates, which necessitates that their synthesis be carried out in an inert atmosphere. Moreover, pure copper(I) β -diketonates are unstable and undergo disproportionation even at relatively low temperatures.²⁷⁵ This can be prevented by additional complexing of the coordination-unsaturated copper atom with various ligands (Lewis bases).

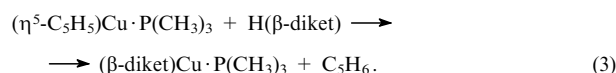
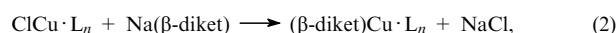
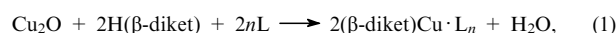
Various organic and inorganic compounds (carbon monoxide, alkynes, dienes, phosphines, amines) forming volatile complexes $(\beta\text{-diket})\text{Cu} \cdot \text{L}_n$ can be used as additional ligands. The additional ligand is eliminated upon disproportionation of the complex to give a volatile neutral compound



Of numerous compounds of this type synthesised to date, only compounds with H(HFA) satisfy the CVD process requirements. Derivatives of other β -diketones are generally insufficiently stable or do not provide reproducible results in the film synthesis. For example, rather stable complexes of Cu(acac) with trimethylsilylalkynes and trimethylsilylalkadiynes were obtained. These complexes were suggested as volatile CCC,²⁷⁶ but CVD processes based on them have not been carried out.

We believe that the problem of stability of complexes with copper(I) β -diketonates, in particular with Cu(HFA), with additional ligands is a key problem for the evaluation of their possible use as the starting CCC in CVD technology. Thermodynamically stable complexes with high activation energies of thermolysis upon film deposition require high substrate temperatures or additional energy sources (plasma, laser radiation); this diminishes the advantages of these CCC over similar copper(II) β -diketonates which are much more readily accessible synthetically. Cu(I) complexes of low stability cannot provide the deposition efficiency and the process reproducibility. Hence, there should be a certain optimum degree of stabilisation of the Cu(HFA) molecule by virtue of the π -donor ability of a Lewis base used as the additional ligand. In fact, of all $\text{Cu}(\text{HFA}) \cdot \text{L}$ complexes synthesised, derivatives considered as potential starting CCC for CVD processes include those which contain moderately strong π -donors (*e.g.*, phosphines rather than amines) or compounds in which the π -donor ability of the multiple bond is somewhat weakened due to the incorporation of π -accepting trimethylsilyl groups [trimethylvinylsilane, bis(trimethylsilyl)acetylene].²⁷⁷

To date, several methods for the preparation of complexes of copper(I) β -diketonates with Lewis bases have been described. These include direct reaction with copper(I) oxide, the exchange reaction with sodium β -diketonates and metallation of β -diketonates with monovalent copper compounds.^{278–282}



Each of these variants involves certain synthetic difficulties. For example, reaction (1) is, technically, the simplest method.²⁸² However, water formed in the reaction favours undesirable disproportionation during the synthesis. In addition, it is difficult

to monitor the stoichiometry of the products in this method.²⁸³ The order of addition of the reagents is very important, since the formation of free Cu(I) β -diketonate, which undergoes disproportionation below 78 °C, should not be allowed. This is avoided by using an excess of the Lewis base.

The additional problem in method (2) involves the presence of sodium cations, which can appear as admixtures in the films obtained from the CCC synthesised using this approach.¹¹¹ The presence of these admixtures is absolutely unacceptable.

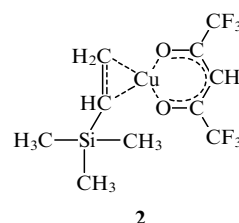
The reaction according to the pathway (3) occurs without complications; however, the cyclopentadienyl complex of copper(I) required is the least accessible potential starting compound of all three pathways.

a. Complexes of Cu(I) β -diketonates with alkenes and alkenylsilanes

The stabilising effect of the double bond in alkenes with respect to copper(I) β -diketonates is generally sufficient for the formation of stable complexes that can serve as the starting CCC. This is exemplified in the complex of (HFA)Cu(I) with vinylcyclohexane (VCH) synthesised²⁸⁴ according to the procedure described previously.²⁸² Unfortunately, data on the physicochemical properties of this compound were not reported. The substrate temperature during the film deposition was 100–175 °C, which is lower than the temperatures for other CCC. The copper films obtained had low SER and virtually did not contain admixtures.

Of copper(I) derivatives stabilised by double bonds of the additional ligand, complexes of Cu(HFA) with alkenyltrimethylsilanes are among the most promising compounds for the synthesis of copper films.

It is known that the trimethylsilyl group manifests a significant π -acceptor effect²⁷⁷ which is unfavourable for the coordination of the adjacent C=C bond of the alkene with the monovalent copper ion. In fact, the compound Cu(HFA) with the simplest alkenyltrimethylsilane, *viz.*, vinyltrimethylsilane (VTMS) **2** first described in 1991,²⁸⁵ is readily oxidised in air to give copper(II) derivatives and is quickly decomposed at ~ 150 °C.²⁸⁶



The decomposition of (HFA)Cu(VTMS) was noted even on storage of this compound at room temperature.²⁸⁷ However, these drawbacks are compensated by the fact that this compound is a volatile liquid even at 20 °C. The vapour pressure of (HFA).Cu(VTMS) is 0.14 Torr at 30 °C (see Ref. 288) and 0.3 Torr at 40 °C (see Ref. 289) and is considerably higher than the similar parameter for $\text{Cu}(\text{HFA})_2$ up to 95 °C.²⁸⁵

The thermolysis activation energies of (HFA)Cu(VTMS) for various deposition conditions and substrate materials have been reported.^{290,291} Various aspects of substrate surface pretreatment for maximising the deposition efficiency of copper films from this compound were studied in detail for TiN.^{292–296} The best characteristics of copper films obtained from vapour on this widespread material were achieved on substrate surfaces pretreated with WF_6 vapour.²⁹⁵

On the whole, the CVD process involving (HFA)Cu(VTMS) has been studied rather thoroughly. An inert gas (He, Ar, N_2) or its mixture with H_2 was used as a carrier gas in most cases. It was shown²⁸⁸ that the deposition rate of copper films increases with increase in the partial pressure of CCC vapour, reaching a maximum (36 nm min^{-1}) at a pressure of 5.7 mTorr. The SER of the copper films was $\sim 2.2 \mu\Omega \text{ cm}$ at thicknesses $> 500 \text{ nm}$. Similar values were obtained under the same or similar conditions in other studies.^{297,298}

As mentioned above, the presence of a reducing gas (H_2) in the thermolytic disproportionation of copper(I) derivatives is generally unnecessary. Nevertheless, it was noted²⁹⁶ that the characteristics of copper films can be improved essentially by additional annealing at 450 °C in a stream of Ar/H_2 (9:1). This increases the grain size in the films, and their SER is decreased from 2.35 to 2.12 $\mu\Omega$ cm.

Various aspects of the favourable effect of hydrogen as the carrier gas in the CVD process based on (HFA)Cu(VTMS) were considered by Lin and Chen.²⁹⁹ It was shown that the use of H_2 provides denser copper films with lower SER values and increases the deposition rate. The film deposition rate can be increased additionally by substrate surface pretreatment with nitrogen plasma.

Braeckelmann *et al.*³⁰⁰ studied the effect of the TiN substrate temperature in the range from 165 to 205 °C on the characteristics of copper films obtained from (HFA)Cu(VTMS) vapour. It was shown in particular that an increase in temperature decreased the SER of copper films from 2.15 to 1.8 $\mu\Omega$ cm and increased the deposition rate by a factor of 2.5. This is attributed to an increase in the CCC disproportionation rate. However, it was shown in a study of a similar process on W/Si substrates³⁰¹ that the SER of the copper films obtained in the substrate temperature range from 160 to 190 °C remained virtually unchanged. The temperature of 190 °C was found to be the optimum providing the maximum film growth rate (up to 500 nm min⁻¹).

It was found in a study of the deposition of copper films on a TiN substrate from (HFA)Cu(VTMS) vapour in a wider temperature range (from 160 to 330 °C)²⁹⁰ that below 200 °C the SER of the films is ~ 2.0 $\mu\Omega$ cm. An increase in the temperature sharply impairs the morphology of the films and increases their SER.

In addition to the substrate temperature, the partial pressure of the starting CCC vapour is an important factor determining the deposition rate and the resulting copper film parameters. A study of the deposition of copper films from (HFA)Cu(VTMS) vapour (TiN/Ti/Si substrate at a temperature of 170 °C) at an overall pressure of 0.5 Torr showed^{302,303} that under these conditions, an increase in the partial pressure of CCC vapour to 0.048 Torr increased the deposition rate monotonically up to 25 nm min⁻¹, and the SER of the film decreased monotonically to 2.00 $\mu\Omega$ cm. With an increase in the partial pressure, the copper films became denser and had fewer surface defects. At partial pressures of (HFA)Cu(VTMS) vapour above 0.048 Torr, the deposition rate and the SER of copper films became virtually constant.

A similar dependence was obtained by Awaya and Arita.³⁰⁴ It was shown that at temperatures below 200 °C, the rate of deposition of copper films from (HFA)Cu(VTMS) vapour is proportional to the square root of the CCC vapour partial pressure.

It was noted above that if copper(II) derivatives [for example, $Cu(HFA)_2$] are used in CVD process, the addition of water vapour to the carrier gas increased the growth rate of copper films while their SER remained unchanged, and in some cases (not always) also increased the process selectivity.^{171, 190, 205, 225, 226} Similar effects were reported for (HFA)Cu(VTMS).

Deposition of copper films from (HFA)Cu(VTMS) vapour on SiO_2 and Pt/ SiO_2 substrates at 150–250 °C gave copper films 800 nm thick with low SER in the absence of water vapour.³⁰⁵ The addition of water vapour did not accelerate the process in the case of the SiO_2 substrate. In the case of Pt/ SiO_2 substrates, a small increase in the deposition rate was observed, but much smaller than that with the use of copper(II) derivatives under the same conditions. The copper films obtained in the presence of water vapour had rough surface structure and high SER (> 20 $\mu\Omega$ cm).

More successful experiments on the deposition of copper films from (HFA)Cu(VTMS) vapour in the presence of water were carried out by Gelatos *et al.*²⁸⁹ It was shown that at rather low partial pressure of water vapour (< 0.4 Torr), as in the case of $Cu(HFA)_2$ vapour, a sharp increase in the copper film deposition rate was in fact observed. This effect was particularly well

pronounced at $P_{H_2O} < 0.2$ Torr. The specific electric resistance of the films obtained was 2.3 ± 0.1 $\mu\Omega$ cm. Subsequent annealing decreased the SER to 1.9 ± 0.1 $\mu\Omega$ cm, and the copper films had a considerably higher density than similar films obtained by CVD from (HFA)Cu(VTMS) vapour in the absence of water vapour. It was noted that such a low SER value was reached in the presence of water vapour at a film thickness of 50 nm, while under 'anhydrous' deposition conditions, this required a film thickness of at least 300 nm. An increase in the water vapour partial pressure to 0.75 Torr impairs strongly the characteristics of the films.^{289, 306}

The possibility of optimisation of a CVD process involving (HFA)Cu(VTMS) and water vapour was studied.^{307, 308} An important fact was noted: the preparation of copper films with low SER, good adhesion and high deposition rate requires that the injection of water vapour be carried out quickly in the beginning of the process. Copper films with SER of 1.9 $\mu\Omega$ cm (after annealing), and copper strips 0.4 μ m wide and 1 μ m thick with good characteristics were obtained under these conditions.

The addition of small amounts of H(HFA) vapour in the CVD of copper films from (HFA)Cu(VTMS) vapour can improve substantially the copper film morphology.²²⁹ The presence of the β -diketone favours an accelerated and uniform growth of nucleation centres on the entire film surface, thus protecting it from cracks and roughening. However, the process loses its selectivity completely in this case.

One more variant for the deposition of copper films by the CVD method from (HFA)Cu(VTMS) vapour involves the addition of an excess of liquid VTMS to the starting CCC (40%–60% relative to the volume of the starting CCC) before the evaporation.^{309, 310} This enabled deposition rates of 40–60 nm min⁻¹ to be achieved. It was noted that replacement of the carrier gas by hydrogen did not change essentially the film growth rate.³¹⁰ The mean specific electric resistance of the copper films obtained, with thicknesses from 200 to 1800 nm, was 1.86 $\mu\Omega$ cm; additional annealing of copper films at 600 °C in a high vacuum (10^{-7} Torr) decreased it to 1.76–1.77 $\mu\Omega$ cm.³⁰⁹

Simultaneous use of H(HFA) and VTMS vapour is possible.³¹¹ The H(HFA) vapour increases the copper film deposition rate, and the VTMS vapour accelerates the CCC evaporation.

The rate of copper film deposition increases considerably if a CVD process with the use of (HFA)Cu(VTMS) vapour is carried out with simultaneous application of a shifting voltage of -30 V to the substrate.^{312, 313} This effect is explained by reorientation of the dipole molecules of the starting CCC in the electric field stimulating their adhesion to the substrate.

The decomposition of (HFA)Cu(VTMS) vapour can be additionally promoted [as in the case of copper(II) derivatives as the starting CCC] by radiation. This variant can primarily be used in the preparation of microstructures from this CCC by lithographic methods.

In the study of Ochiani *et al.*,³¹⁴ deposition of copper films from (HFA)Cu(VTMS) vapour was carried out simultaneously with electron lithography. The copper film samples obtained had rather low SER.

The formation of copper films from (HFA)Cu(VTMS) exposed to an electron beam has been studied.³¹⁵ It was found that the energy threshold where decomposition starts is 4 ± 0.5 eV and that decomposition occurs by dissociative electron addition. However, the films obtained by this method are considerably contaminated with carbon, apparently due to decomposition of HFA fragments under these rather drastic conditions.

A study of the preparation of thin copper strips 3 μ m wide by thermal decomposition of (HFA)Cu(VTMS) vapour under argon laser radiation²⁸⁶ showed that in this case, as with $Cu(HFA)_2$ vapour,²²⁵ the addition of water vapour to the vapour of the starting CCC affects favourably the deposition rate and the characteristics of the resulting copper microstructures. The SER values of the best copper strips obtained this way were close to the SER of metallic copper. Similar results were obtained under

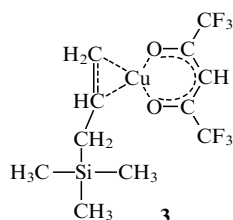
analogous conditions;³¹⁶ it was also noted that the morphology of the surface copper strips depends essentially on the laser radiation power. Moilanen *et al.*³¹⁷ achieved rather high film deposition rates of up to 400 nm s⁻¹, but the SER of the strips increased somewhat (up to 3.7 $\mu\Omega$ cm).

Thin copper strips (channels) up to 16 μ m deep were obtained by CVD using decomposition of (HFA)Cu(VTMS) vapour.³¹⁸ The specific electric resistance of the copper channels was 1.95 $\mu\Omega$ cm; annealing gave a value of 1.86 $\mu\Omega$ cm.

Successful optimisation of preparation of copper strips with SER of ≤ 2.0 $\mu\Omega$ cm using CVD from (HFA)Cu(VTMS) vapour was reported.³¹⁹

Popovici *et al.*³²⁰ observed the terrace growth of copper films during the decomposition of (HFA)Cu(VTMS) vapour on Teflon substrates under excimer laser radiation ($\lambda = 248$ nm). It was assumed that growth of this type occurs owing to the interference between the Teflon support and the precipitated copper layers.

In turn, the successful use of (HFA)Cu(VTMS) vapour as a convenient starting CCC for the CVD process has served as an incentive for the search for volatile Cu(HFA) complexes with similar compositions and physicochemical characteristics. As a result, new starting CCC were reported, where allyltrimethylsilane (ATMS) (for example, compound 3)^{321–323} and vinylalkoxysilanes, such as vinyltrimethoxysilane (VTMOS),²⁸⁷ vinyl(dimethoxy)methylsilane (VDMOMS)³²⁴ and vinyltriethoxysilane (VTEOS),^{324,325} served as Lewis bases. These CCC are more stable than (HFA)Cu(VTMS). They are liquid at room temperature, but data on their physicochemical properties were not reported in these studies.



If (HFA)Cu(VTMS) vapour is used, the optimum temperature range for the TiN substrate, where copper films with the best characteristics are formed, is 175–200 °C.²⁸⁷ The lowest SER of the films obtained under these conditions is 2.5 $\mu\Omega$ cm.

Somewhat better results (deposition rate up to 100 nm min⁻¹ and lower SER of the films) were obtained in CVD processes based on (HFA)Cu(VDMOMS) and (HFA)Cu(VTEOS).^{324,325} It was noted that the presence of water vapour during the deposition of films is necessary for the former compound.³²⁴

Very interesting results were obtained in CVD processes using (HFA)Cu(ATMS). It was found that, other conditions being equal, the incorporation of ATMS in the complex decreases considerably the temperatures for copper film deposition in comparison with those for similar compounds without ATMS. (HFA)Cu(ATMS) evaporates well at 40–45 °C and forms copper films with low SER at substrate temperatures of 60–170 °C.³²¹ It was noted that the film parameters remain almost unchanged in this rather wide temperature range. A certain role in these features of CVD processes is apparently associated with the fact that (HFA)Cu(ATMS) is even less stable thermally than (HFA)Cu(VTMS) and (HFA)Cu(VTMS), and hence it is more reactive.^{323,326} At a temperature as low as 60 °C, the IR spectra of (HFA)Cu(ATMS) vapour contain bands corresponding to Cu(HFA)₂. It is interesting that the morphology of the copper film surfaces obtained also depends on the reactivity of the starting compounds: for example, the grain size in the copper films obtained from (HFA)Cu(ATMS) vapour is much larger than that in the copper films obtained from (HFA)Cu(VTMS) vapour.³²³

b. Complexes of copper(I) β -diketonates with isocyanides

Of copper(I) β -diketonate complexes stabilised by interactions of the copper(I) ion with the double bond, those with *tert*-butyl isocyanide (Bu^tNC) are considered as promising starting CCC for the preparation of copper films by CVD technology. It should be noted that the corresponding complexes of copper(I) derivatives with nitriles RCN decompose even at room temperature.³²⁷ It is known that the nitrile group is an efficient π -acceptor [the resonance constant is $\sigma_R^0 = +0.08$ (see Ref. 277)] and hence it cannot form stable complexes with the copper(I) ion. On the other hand, the corresponding effect of the isocyanide group is close to zero,²⁷⁷ and the additional π -donor *tert*-butyl group makes the complex sufficiently stable.

Kruck and Terfloth³²⁸ reported data on the synthesis [by method (2)] and the physicochemical properties of volatile (HFA)Cu · Bu^tNC and (HFA)Cu · (Bu^tNC)₂ complexes (in particular, the sublimation temperatures at 0.1 Torr are 55 and 95 °C, respectively). CVD processes with the use of vapour of these compounds gave copper films with good characteristics.³²⁹

c. Complexes of copper(I) β -diketonates with dienes

Dienes form rather stable 1 : 1 complexes with the copper(I) ion. Copper(I) β -diketonates are usually stabilised by 1,5-cyclooctadiene (1,5-COD).

Like complexes with VTMS, complexes of 1,5-COD with Cu(acac) and Cu(TFA) have low stability,²⁸² on the contrary, (HFA)Cu(1,5-COD) is a very stable compound which sublimes without decomposition at 65–70 °C and remains unchanged in air for a period of one year. The vapour pressure of this compound is ~ 56 mTorr at 62 °C.³³⁰

The spatial structure of the (HFA)Cu(1,5-COD) molecule (Fig. 3) was determined²⁸² and analysed in detail.²⁸⁰ It was noted in the latter study that the actual coordination of the Cu(I) centre is more complex than Fig. 3 shows and fits a 3 + 1 scheme. In other words, the 1,5-COD fragment is coordinated asymmetrically. Decomposition of vapour of this CCC at 200 °C resulted in copper film formation and evolution of volatile decomposition products, *viz.*, Cu(HFA)₂ and 1,5-COD.²⁸²

The preparation of copper films by CVD from (HFA)Cu(1,5-COD) vapour has been described in a number of papers.^{330–335} For example, it was noted³³⁰ that a temperature of 65 °C in the evaporator and a temperature of 70 °C of the reactor cell walls are sufficient for the process. Admixtures of carbon, oxygen and fluorine are virtually absent in the films (< 1%).

The specific electric resistance of films obtained from (HFA)Cu(1,5-COD) vapour depends primarily on the substrate temperature. At the optimum temperature (190–210 °C), the SER of the films was 1.97 ± 0.10 $\mu\Omega$ cm. Higher deposition rates (> 15 nm min⁻¹) and larger film thicknesses (> 250 nm) worsen this parameter.

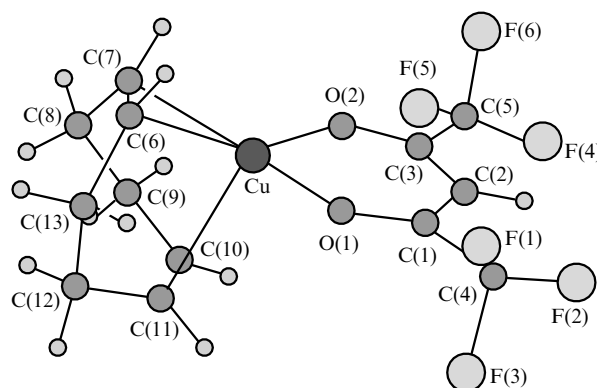


Figure 3. (HFA)Cu(1,5-COD) molecule.

(HFA)Cu(1,5-COD) is a promising starting compound in an aerosol modification of CVD technology.³³⁵ The films are deposited from an aerosol of a toluene solution of the starting compound. The aerosol is fed to the reactor cell in a stream of an inert gas (nitrogen); intermediate preheating of the vapour to 40–100 °C is provided. Even at a substrate temperature of 120 °C, crystalline copper films were obtained; their SER were within 1.7–3.5 $\mu\Omega$ cm under optimum process conditions (140 °C, deposition rate 80 nm min⁻¹).

Copper films with good characteristics are obtained using (HFA)Cu(1,5-COD) as the starting CCC in the presence of CO.³³⁶ Carbon monoxide displaces the 1,5-COD ligand from the complex at -70 °C to give an intermediate unstable carbonyl compound, (HFA)Cu(CO), which in this case serves as the starting CCC in the CVD process. Isolation of this carbonyl complex in a pure state failed.

1,5-COD is not the only diene that can give volatile complexes with copper(I) β -diketonates applicable in CVD technology. In particular, a hydrocarbon which is rare but quite accessible synthetically, *viz.*, 7-*tert*-butoxynorbornadiene 7-Bu'O-NBD, was suggested for this purpose³³⁷ (for its synthesis, see Ref. 338). Using a procedure which is a modification of the method (2), Chi *et al.*³³⁷ obtained a series of complexes of the type (β -diket)Cu(7-Bu'O-NBD), where β -diket = acac, TFA, HFA, FOD, with sublimation temperatures from 75 to 90 °C at 0.1 Torr. The geometry of the molecules was determined for all of these complexes. However, only one of these compounds, namely, Cu(HFA)(7-Bu'O-NBD), was found to be suitable for the preparation of copper films. The specific electric resistance of the films was satisfactory at sufficiently high substrate temperatures; the SER of films increased abruptly (> 1000 $\mu\Omega$ cm) and their surface morphology is deteriorated upon decrease in the temperature of the substrate to 170 °C.³³⁷

d. Complexes of copper(I) β -diketonates with alkynes

It is known that the triple bond, particularly that in alkyl-substituted acetylenes, has a stronger π -donor effect than the double bond.²⁷⁷ Hence, alkynes should form sufficiently stable complexes with the copper(I) atom in β -diketonate derivatives.

The first synthesis of volatile η^2 -complexes of Cu(HFA) with alkynes, *viz.*, but-2-yne, bis(trimethylsilyl)acetylene and diphenylacetylene, was carried out by the reaction of (HFA)Na with CuCl in the presence of excess alkyne.²⁷⁸ Volatile Cu(HFA) complexes with pent-2-yne³³⁹ and hex-3-yne³⁴⁰ were also obtained. A little later, a simple one-stage procedure was proposed for the synthesis of Cu(HFA) complexes with but-2-yne³⁴¹ and bis(trimethylsilyl)acetylene.³⁴² A series of compounds of this class containing silicon atoms at the triple bond were patented as the starting CCC for CVD technology.³⁴³

According to X-ray diffraction data, the copper(I) atom in the compounds in question has a flat trigonal configuration with coplanar diketonate and alkyne ligands (Fig. 4).²⁷⁸ The nature of bonding and the electron interaction of the fragments in this type of complex was studied in more detail using ¹H and ¹³C NMR spectroscopy.^{281, 342}

The possibility of the existence of equilibrium between mononuclear and binuclear forms of these complexes was also considered,³⁴² as some of them undergo chemical transformations in the bubbler of the CVD reactor at 45–65 °C to give low-volatility products.^{340, 341} In this case, the corresponding binuclear complexes are obviously formed by μ - η^2 bonding of the triple bond with the copper atom [the ratio alkyne: Cu(HFA) = 1 : 2]. Such complexes are also known in the chemistry of other transition metals.^{344, 345} However, in this case the complexes are extremely unstable³⁴² and can only be formed as labile intermediates. On the whole, the nature of this reaction has been studied insufficiently.

The Cu(HFA) complex with but-2-yne is decomposed on the substrate at 150–210 °C under the conditions of the CVD process to give dense mirror-like copper films with low SER.³³⁹ The rate of deposition of such films can be increased by addition of water

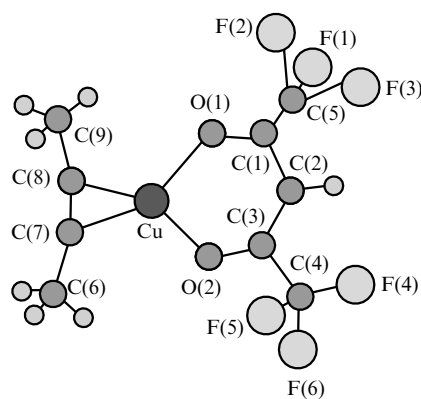


Figure 4. (HFA)Cu(CH₃C≡CCH₃) molecule.

vapour.³⁰⁶ The possibility of selective deposition of copper films starting from this compound was considered.³⁴⁶

An unusual modification of this type of the starting CCC was suggested by Schmidt and Behrens.³⁴⁷ They synthesised a volatile 2 : 1 Cu(HFA) complex with bis(*tert*-butylethynyl) sulfide. It was shown that the sulfur atom did not participate in coordination with the copper(I) ion. Similar Cu(I) complexes with other β -diketonates as the ligands were found to be unstable even at room temperature.

e. Complexes of copper(I) β -diketonates with phosphines

Yet another possibility to stabilise Cu(HFA) is the preparation of its complexes with derivatives of VA Group elements. Of these derivatives, trialkylphosphines are used most widely as additional ligands. However, the volatility of biscomplexes of the type (β -diket)Cu(PAlk₃)₂ synthesised first³⁴⁸ was insufficient for their use in CVD technology.

The syntheses of volatile monomeric 1 : 1 complexes of copper(I) β -diketonates with organic phosphines for CVD were first reported by Shin *et al.*^{349–351} Initially, the reaction according to pathway (3) became the main method for their synthesis;³⁵¹ the applicability of pathway (2) was shown later.^{279, 352} The compounds obtained were low-melting crystals capable of sublimation or viscous liquids.

As in the case of similar complexes with 1,5-COD,²⁸⁰ the HFA derivative (Fig. 5) was the most stable of the series of compounds with the general formula (β -diket)Cu(PMe₃), where β -diket = acac, TFA, HFA.

The same is true for complexes with other trialkylphosphines.³⁵² To interpret this phenomenon and to study the nature of the interaction of the copper(I) ion with the phosphine molecule, photoelectron spectroscopic data and quantum-chemical calculations were used.³⁵³

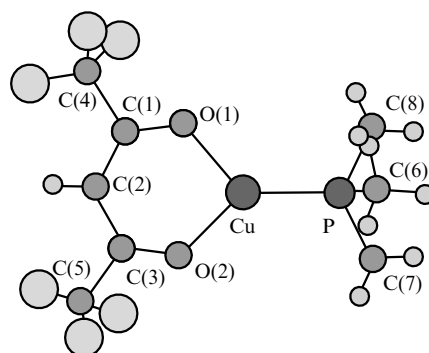


Figure 5. (HFA)Cu(PMe₃) molecule.

The vapour pressure of $\text{Cu}(\text{HFA})(\text{PMe}_3)$ was measured at various temperatures and the $\log P - 1/T$ relationship was plotted.²⁷⁹ The corresponding vapour pressures of $\text{Cu}(\text{HFA})(\text{PMe}_3)$ and $\text{Cu}(\text{HFA})_2$ were found to be similar.¹⁷⁹

The first experiments on CVD of thin films with the use of phosphine complexes of copper(II) β -diketonates as CCC gave promising results. For example, a rather high deposition rate (up to 100 nm min^{-1}) was achieved at 150°C on a Pt/SiO_2 substrate resulting in dense mirror-like copper films with good adhesion.³⁵⁴ It was reported that the process can occur selectively.³⁵⁰ A more detailed study showed that phosphine complexes of $\text{Cu}(\text{HFA})$ have higher selectivity than similar complexes with 1,5-COD or alkynes under comparable conditions.

Thin copper films were also deposited from $\text{Cu}(\text{HFA})(\text{PMe}_3)$ vapour in the presence of water and organic solvents (alcohols, toluene, tetrahydrofuran).²⁰⁶ It was shown that this compound can react with water at room temperature with partial oxidation of copper(I) to copper(II). The use of alcohols results in reversible coordination of the alcohol molecules with copper(I) ions with formation of a more volatile alkoxide and, hence, leads to an increase in the deposition rate of copper films.

2. Volatile compounds of copper(I) devoid of β -diketonate ligands

A series of volatile derivatives of monovalent copper includes CCC which are not inferior to β -diketonates in terms of physicochemical properties required in CVD technology. Such CCC can be considered as alternatives to the classical β -diketonate copper(I) complexes. An obvious direction of the molecular design of such compounds is some structural similarity to copper β -diketonates. In view of this, we included copper β -iminoketonates and β -oxocarboxylates in our consideration.

Yet another direction in the creation of new CCC is the search for fragments capable of replacing completely the β -diketonate group while preserving the properties needed for CVD technology. The promising compounds of this type include alkoxides, amides, cyclopentadiene derivatives and heterocyclic compounds (e.g., pyrazole derivatives).

a. Copper(I) β -iminoketonates and β -oxoacid derivatives

Fluorinated β -iminoketonates required for the synthesis of stable nitrogen-containing analogues of copper(I) β -diketonates are obtained by a two-step procedure from the corresponding β -diketonates.³⁵⁵ This fact itself implies the low competitiveness of copper(I) β -iminoketonates synthesised from sodium β -iminoketonates by reaction (2) in comparison with similar copper(I) β -diketonates.

At room temperature, complexes of this series (with trialkylphosphines as additional ligands) are volatile liquids or solid compounds. A study of whether copper films can be obtained by CVD from vapours of copper(I) β -iminoketonates did not reveal any considerable advantages of these compounds over the more accessible oxygen analogues,^{355, 356} i.e., copper(I) β -diketonates. Only one study was published³⁵⁷ reporting good results in the preparation of copper films by CVD with the use of a complex of copper(I) 3-oxobutanoate with trimethylphosphine which is rather stable and resistant against oxidation in air.

b. Copper(I) alkoxides

The main drawback of copper(I) alkoxides as potential CCC for CVD technology is their rather easy transition into non-volatile polymers. Nevertheless, successful attempts at the preparation of copper films from tetrameric copper(I) *tert*-butoxide $[\text{Cu}(\text{OBu}^t)]_4$ were reported.^{358, 359} The pyrolysis temperature of this compound is rather high ($\sim 400^\circ\text{C}$). As indicated by Lemmen *et al.*,³⁶⁰ this compound is rather sensitive to oxygen and atmospheric moisture (the films obtained contained from 2% to 5% of oxygen), therefore it was not widely used in CVD technology.

Hampden-Smith *et al.*³⁶¹ synthesised a volatile monomeric complex of copper(I) *tert*-butoxide with trimethylphosphine

$(\text{Bu}^t\text{O})\text{Cu}(\text{PMe}_3)$. The CVD method made it possible to obtain pure copper films containing no oxygen and phosphorus admixtures from this compound.³⁶¹

c. Amide derivatives of copper(I)

In the series of volatile amide derivatives of copper(I), there is one unusual compound used as a CCC, *viz.*, the tetrameric cluster $\{\text{Cu}[\text{N}(\text{SiMe}_3)_2]\}_4$.³⁶² This compound sublimes at rather high temperature ($\sim 180^\circ\text{C}$). Nevertheless, it produces copper films with satisfactory characteristics. It is possible that further research on copper(I) amide derivatives will allow one to obtain compounds of this class that would be more volatile and, accordingly, more promising for CVD technology.

d. Cyclopentadienyl derivatives of copper(I)

Cyclopentadienyl derivatives of copper(I) compete satisfactorily with copper β -diketonates as starting compounds in CVD processes. Cyclopentadienyl derivatives of copper(I) are usually stabilised by trialkylphosphines and isocyanides.

Trialkylphosphine complexes of cyclopentadienylcopper(I) are usually synthesised using a procedure similar to the pathway (2) from cyclopentadienylsodium and halophosphine complexes of copper(I).^{363, 364} Their typical sublimation temperatures are $60\text{--}70^\circ\text{C}$, and the thermal decomposition temperatures are $120\text{--}125^\circ\text{C}$.³⁶⁵ The calculated vapour pressure of $(\text{Cp})\text{Cu}(\text{PMe}_3)$ at 80 and 100°C are 14 and 30 Torr, respectively.⁷

For similar platinum compounds, it was found that incorporation of a methyl group in the cyclopentadiene ring increases considerably the volatility of the compound.³⁶⁴ In view of this, copper(I) methylcyclopentadienyl complexes with trialkylphosphines were synthesised,³⁶³ but their sublimation temperatures and vapour pressures were almost the same as those of the non-substituted analogues. A study of the physicochemical properties showed that the methyl-substituted derivatives are less stable and undergo decomposition at temperatures $15\text{--}20^\circ\text{C}$ lower than the non-substituted compounds. This is an advantage of methyl-substituted cyclopentadienyl derivatives of copper(I) for the CVD process. Recently, a number of methyl- and ethyl-substituted cyclopentadienyl complexes of copper(I) with triisopropylphosphine were patented as promising volatile CCC for CVD technology.³⁶⁶

Originally, such complexes were used in CVD for the synthesis of mixed copper-containing semiconductor systems of the CuGaS_2 type.³⁶⁵ The first studies on the CVD of copper films with the use of these complexes gave good results. For example, it was shown³⁶⁷ that decomposition of $(\text{Cp})\text{Cu}(\text{PAlk}_3)$ vapour (Alk = Me, Et, Bu) on substrates made of different materials *in vacuo* gave high-purity copper films with a SER that differed from the SER of bulk metallic copper by $\sim 10\%$. Based on $(\text{Cp})\text{Cu}(\text{PMe}_3)$, copper films with SER of $1.8\text{--}2.2 \mu\Omega \text{ cm}$ were obtained,³⁶¹ but this value was achieved only after annealing. The morphology of the surface of copper films formed from $(\text{Cp})\text{Cu}(\text{PET}_3)$ vapour on SiO_2 was considered in detail.³⁶⁸

The $(\text{Cp})\text{Cu}(\text{PET}_3)$ complex was used as the starting CCC in laser-activated preparation of copper strips and in thermal laser lithography.³⁶⁹ Irradiation of a thin layer of this compound with the light of an argon laser at $\lambda = 514 \text{ nm}$ gave a copper strip containing less than 10% carbon and with SER of $\sim 6.8 \mu\Omega \text{ cm}$. The use of radiation excimer lasers with shorter wavelengths resulted in strips of copper-carbon composites.

The $(\text{Cp})\text{Cu}(\text{PET}_3)$ complex was used for the CVD synthesis of thin copper-aluminium films *in situ*.⁷ In this method, the rather low concentration of copper ($\sim 1.4\%$) decreases greatly the SER of the basic aluminium film. The valuable property of $(\text{Cp})\text{Cu}(\text{PET}_3)$ is that, unlike the majority of the starting volatile CCC, it is chemically inert with respect to the second aluminium-containing starting compound used simultaneously, *viz.*, dimethylalane $(\text{CH}_3)_2\text{AlH}$.

As in the case of $\text{Cu}(\text{HFA})$, *tert*-butyl isocyanide can be used for the stabilisation of copper(I) cyclopentadienyl complexes. The

(Cp)Cu(Bu⁴NC) compound was obtained for the first time using method (1) and was used as a catalyst of some organic reactions.³⁷⁰ Later, this substance was synthesised using method (2) and was suggested as a starting CCC for the preparation of copper films by CVD.³²⁸ Studies of the behaviour of this compound in CVD showed^{329,371} that high-quality films free from carbon admixtures can in fact be obtained on its basis. The optimum substrate temperature range is 200–350 °C,³⁷¹ although noticeable decomposition of (Cp)Cu(Bu⁴NC) starts at 135 °C.³²⁸

e. Complexes of copper(I) with pyrazole derivatives

Many volatile compounds are known in which the copper(I) ion is bound to heterocyclic fragments. However, only one study is devoted to the synthesis of copper(I) pyrazolyl borate complexes with triethylphosphine.³⁷² At a substrate temperature of 150 °C, these compounds give polycrystalline copper films with good characteristics and high selectivity. Apparently, studies in this direction will continue.

3. Mechanisms of decomposition of copper(I) derivatives on the substrate

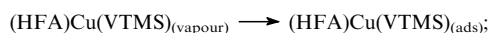
It is generally believed that copper films are formed from mono-valent copper–HFA complexes due to their disproportionation followed by removal of the volatile product. The formation of Cu(HFA)₂ from (HFA)Cu(VTMS) in the gas phase was proved by spectral methods.^{189,373}

The initial step of (HFA)Cu(VTMS) decomposition should apparently involve cleavage of the weakest bond in the molecule, *i.e.*, the bond between the copper(I) ion and the VTMS molecule. The question is, where does this cleavage occur? There are two answers to this question: first, on the substrate surface; second, in the vapour phase. Evidence in favour of both variants can be found in the literature.

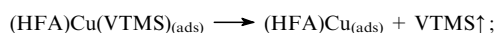
The majority of the authors favour the first variant.^{201,290,374} For example, a comparative study of the Cu(HFA)₂ and (HFA)Cu(VTMS) decomposition by Fourier IR spectroscopy revealed bands unambiguously assigned to the VTMS ligand in the spectra of (HFA)Cu(VTMS) adsorbed on a Si(100) substrate at –148 °C.²⁰¹ However, these bands disappeared at 27 °C, which made it possible to conclude²⁰¹ that at this temperature VTMS was eliminated extremely quickly from the adsorbed compound. The disproportionation of the resulting Cu(HFA) molecules was proved and considered in detail.^{310,374–376}

Thus, taking this into account, one can make the conclusion that the most probable mechanism of decomposition of (HFA)Cu(VTMS) vapour involves four steps:

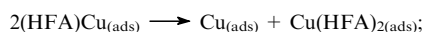
(1) adsorption of the entire molecule on the substrate



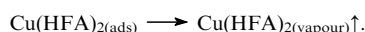
(2) elimination of VTMS followed by fast desorption



(3) bimolecular disproportionation of the intermediate formed

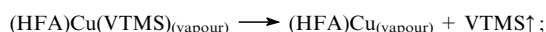


(4) desorption of the volatile product of Cu(HFA)₂ disproportionation

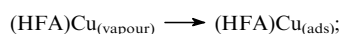


However, studies of the kinetics of (HFA)Cu(VTMS) decomposition³⁷⁷ gave evidence in favour of the second variant, *i.e.*, molecular decomposition in the vapour phase. Hence, it is the intermediate Cu(HFA) that should be considered the actual starting compound in the copper film formation. The second mechanism, alternative to the one mentioned above, is as follows:

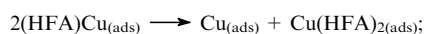
(1) vapour-phase thermolysis



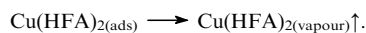
(2) adsorption of the intermediate



(3) bimolecular disproportionation of the intermediate formed



(4) desorption of the volatile product of Cu(HFA)₂ disproportionation



The third and fourth steps are similar in both cases.

It is possible that bimolecular disproportionation (third step) is not the only pathway for the transformation of the Cu(HFA) intermediate. A direct relationship between the activation energy of the copper nucleation from (HFA)Cu(VTMS) on the surface and the electric conductivity of the substrate was established; this is believed³⁷⁸ to suggest a certain role of one-electron transfer from the surface to the adsorbed Cu(HFA), which was not taken into account in the mechanism considered above.

One can imagine a situation (for example, at a sufficiently high temperature of the vapour flow) where a portion of molecules of the starting CCC are decomposed in the vapour phase, while the other portion do so on the substrate surface. The relative fractions of each process depend on the particular conditions of the process.

The effect of the substrate temperature on the mechanism of low-vacuum deposition of the copper film from the (HFA)Cu(VTMS) vapour was studied in detail.²⁹⁸ It was shown that in the temperature range of 140–220 °C, deposition obeys the Arrhenius law; at temperatures higher than 220 °C, the process switches to the saturation mode (the ‘transport-limited’ situation). In this mode, the SER of the film and the content of contaminating carbon increase.³⁷⁹ In addition, the film formed becomes less uniform due to a decrease in mobility of copper atoms under the effect of the atoms of the quickly growing surface layers.³⁸⁰

The mechanism of the effect of partial pressure of (HFA)Cu(VTMS) vapour on the characteristics of films considered by Lee *et al.*³⁰² fits completely the deposition scheme described above. At low partial pressure of CCC vapour, the sites for the adsorption of the Cu(HFA) intermediates are preserved on the substrate surface. As the pressure is increased to a certain threshold, the surface becomes ‘adsorption-saturated’ and the copper film deposition rate no longer depends on the partial pressure.

As in a case of Cu(HFA)₂, a special situation arises if CVD is carried out with the use of (HFA)Cu(VTMS) under ultrahigh vacuum (10^{–9}–10^{–10} Torr).¹⁹⁹ Under these conditions, the first stage involves chemisorption of the entire CCC molecule on the substrate (TiN). At 27 °C, the CCC is completely transformed to the adsorbed Cu(HFA) intermediate, which does not disproportionate upon heating but is decomposed to CO, CO₂, CF₄ and metallic copper. About 90% of the copper contained in the precursor remains on the substrate [~30% in the case of Cu(HFA)₂ under the same conditions]. At 280 °C, the diffusion of copper into the substrate starts.

It is believed³⁰⁶ that the favourable effect of water vapour on the deposition rate of copper films upon decomposition of (HFA)Cu(VTMS) vapour is associated with facilitation of the VTMS ligand elimination. The observed impairment of the characteristics of copper films at high partial pressure of water vapour^{289,306} occurs because of the side reaction of water with the adsorbed Cu(HFA) intermediate resulting in a Cu₂O admixture in the films. Experiments with water labelled with the ¹⁸O isotope showed that it is the oxygen atoms from water molecules that are incorporated in the film.³⁰⁶

A mechanism of (HFA)Cu(VTMS) decomposition under ion beam impact to give copper films has been suggested.³⁸¹

The decomposition mechanism of other copper(I) derivatives, such as Cu(HFA)(1,5-COD), and Cu(HFA) complexes with but-

2-yne on a silicon substrate during the CVD process ($\sim 210^\circ\text{C}$) is totally similar to the mechanism considered above^{375, 382} (including that in the presence of water vapour³⁰⁶). However, there are no data on the elimination of additional ligands (Lewis bases) from these compounds directly in the vapour phase.

The mechanisms of transformations in thin copper films during their subsequent annealing^{289, 309} have not been elucidated so far. The available data on the effect of annealing on the characteristics of films are rather contradictory. For example, it was reported that annealing of films decreased their SER considerably,^{289, 383} decreased it slightly³⁰⁹ or did not affect it.³⁸⁴ This could result from processes affecting the SER in opposite ways: annealing increases the film crystallinity and, on the other hand,

favours their oxidation and enhances the diffusion of copper atoms into the substrate material.³⁸⁵

The mechanism of thermal decomposition of the vapour of copper(I) *tert*-butoxide tetramer on the substrate was studied in detail.³⁵⁹ It was shown that a homolytic process results in intermediate *tert*-butyl radicals and copper(I) oxide; the effect of the latter can explain the presence of oxygen in the films obtained. On the other hand, thermal decomposition of a vapourised phosphine complex of copper(I) *tert*-butoxide did not result in either the formation of Cu_2O or an admixture of oxygen in the films. Data on the deposition conditions of copper films from copper(I) derivatives and the corresponding SER values are listed in Table 5.

Table 5. CVD conditions and properties of copper films obtained from copper(I) compounds.

Starting CCC	$T/^\circ\text{C}$	P/Torr	Barrier layer	Substrate	$T_p/^\circ\text{C}$	Carrier gas	SER/ $\mu\Omega\text{ cm}$	Ref.
(HFA)Cu(VCH)	45–55		TiN	Si	100–175	Ar	1.9–2.3	284
(HFA)Cu(VTMS)	—		TiN	Si	200–250		1.9–2.3	289
—	—		TiN	Si	165–205	H_2O	1.8–2.06	300
—	—		W, SiO_2 ,	CoSi_2	160–300		—	291
—	—		TiN	Si(100)	300	H_2O , H_2	—	260, 308
—	—		—	Si		H(HFA), VTMS	1.8	311
—	0.5		Si_3N_4	Si	220–250	VTMS, N_2	1.82–1.86	309, 310
—	—		W, TiN,	Al	140		—	386
—	0.12		TiN, TiW	SiO_2	200	Ar/ N_2	3–10	387
—	—		SiO_2	Pt, SiO_2		H_2O	> 20	305
—	—		W,	SiO_2 , Si		H_2O	2.0–12.0	306, 388
—	—		TiN,	SiO_2 , Si	< 200		2.0	290
—	—		TiN	Si	150–200 ^a	N_2	1.8	389
—	0.12		—	Si	150–200 ^a		3.6	314
—	—		—	Si	150–200 ^b		—	316
—	—		TiN	Si	150–200 ^c	H_2	—	206
—	—		Si_3N_4 , SiO_2	—	150–200 ^b		3.7	317
—	50	2	TiN	Si	100–300	Ar	—	379
—	—		TiN, Ti	Si	180		2.35	296
—	40	0.5	TiN, TiW	Si	170	He	2.0	302
—	—		—	SiO_2 , Pt	225		—	378
—	—		—	Si	150–250	H_2	—	390
—	33	0.06	TiN, TiW	Si	130–180	H_2	2.2–2.3	288
—	70–80	—	TiN	Si	120–180		—	377
—	—		TiN	SiO_2	75–250		2.0	284
(HFA)Cu(ATMS)	40–45	—	TiN	Si(100)	60–170		1.7–1.9	321
—	60–90	—	—	Si	275		2.0	322
(HFA)Cu(VDMOMS)	—	—	—	Si	195	H_2O	2.0	324
(HFA)Cu(VTEOS)	—	—	—	Si	195		2.0	324
—	70–80	—	—	Si(100)	180–220	N_2	2.0	325
(HFA)Cu(VTMOS)	60–65	—	TiN	Si	175–200	Ar	2.5	287
—	—		TiN	Si	160–220		—	351
(HFA)Cu(1,5-COD)	62	0.07	—	Si	190–210		1.97 $\pm$ 0.10	330
—	—		Ag	Si(111)	180–300		2.0–2.4	334, 375
—	—	760	SiO_2	Si, W	140	N_2	1.7–3.5	335
(HFA)Cu(7-Bu'O-NBD)	—	—	—	Pt, SiO_2	> 200		< 6	337
(HFA)Cu($\text{CH}_3\text{C}\equiv\text{CCH}_3$)	—	—	SiO_2	Si	210		2.0	339
(Bu'O)Cu(PMe ₃)	—	—	Pt	SiO_2	260–450		10–12 (1.8–2.2) ^c	361
(Cp)Cu(PMe ₃)	—	—	W, SiO_2	Si ^d	150–220		2.0	367
—	—	—	—	Pt, SiO_2	260		1.8–2.2 ^c	361
(Cp)Cu(PET ₃)	—	—	W, SiO_2	Si	150–220		2.0	363, 367
—	66	400	SiO_2	Si(100)	280–550	H_2	—	368
—	—	—	SiO_2	Si	280–550 ^b		6.8	369
(Cp)Cu(PBu ₃)	—	—	W, SiO_2	Si ^d	150–220		2.0	367
[CuN(SiMe ₃) ₂] ₄	180	0.2	—	Si	145	H_2	—	362

^a Under a 30–50 keV electron beam. ^b Under argon laser irradiation. ^c Under krypton laser irradiation. ^d Other supports were also used. ^e After annealing of the films at 600°C .

VI. The problem of selective deposition of copper films

The selectivity of deposition of copper films by the CVD method from the vapour of copper(II) and copper(I) derivatives deserves a separate discussion. Let us note the short reviews^{391,392} on the subject.

The selectivity of deposition implies preferential growth of the copper film on the surface of a certain material relative to the surface of some other material. This problem is important because at the present time there are no versatile methods for etching copper films covering the entire surface of a sample, which would allow one to obtain predetermined shapes on the surface required in the production of microelectronic devices.

For example, a method for the dry etching of copper by consecutive treatment of its surface with H_2O_2 (which oxidises copper to Cu_2O) and $\text{H}(\text{HFA})$ (which transforms Cu_2O into a volatile copper β -diketonate) was suggested.³⁸⁸ A similar idea was implemented by Steger and Masel³⁹³ who used $\text{H}(\text{HFA})$ vapour in a stream of O_2 . However, though high etching rates were achieved [$\sim 1000 \text{ nm min}^{-1}$ at 190°C (see Ref. 388) and $\sim 1500 \text{ nm min}^{-1}$ at 350°C (see Ref. 393)], these techniques did not become popular. This is also true for the other known etching methods requiring rather drastic conditions, such as a method with the use of SiCl_4 in a stream of N_2 ($T > 250^\circ\text{C}$)³⁹⁴ and treatment with a mixture of chlorine and PEt_3 vapour in the presence of $\text{H}(\text{HFA})$ at $420\text{--}540^\circ\text{C}$.³⁹⁵

1. Deposition of copper films in 'metal–dielectric' systems

As a rule, SiO_2 is used as a dielectric for the deposition of copper films in 'metal–dielectric' systems.

The growth of a copper film on a dielectric substrate surface primarily depends on the ease of adsorption of molecules of volatile CCC and compounds accompanying the process on the surface. The growth step following adsorption is nucleation, *i.e.*, formation of primary grains of the growing film at the sites where adsorption is the most efficient and where decomposition of molecules of the CCC mostly starts. It was assumed that it is this step that determines the overall process selectivity.³⁸⁷

Hence, the simplest solution for the selectivity problem can involve suppressing the nucleation³⁹⁶ or providing conditions where adsorption of molecules of the CCC on the dielectric surface is suppressed, while that on the metal surface is not suppressed. However, this solution also involves certain difficulties. The main of these results from the fact that, depending on the deposition conditions (temperature, pressure, carrier gas), the adsorption of molecules of CCC can be either physical or chemical.²⁰³ Therefore, a versatile method for the treatment of SiO_2 substrate surfaces in order to minimise adsorption and achieve the maximum selectivity obviously cannot exist: everything depends on the particular CVD technology and the CCC used.

The nature of selectivity in the deposition of copper films from $\text{Cu}(\text{HFA})_2$ vapour on Ag/SiO_2 substrates was considered in detail by Cohen *et al.*³⁷⁶ It was assumed that selectivity is provided due to the existence of several paths of the CVD process: on the surface of silver, fast reduction of copper(II) to copper(I) occurs with desorption of the HFA ligand due to electron transfer from the metal surface, whereas on the surface of the SiO_2 dielectric, the molecules of the starting CCC are adsorbed in the original state.

The consecutive growth of film layers relative to the dielectric substrate can be regarded as a particular case of the above scheme. Deposition of copper films by decomposition of $\text{Cu}(\text{HFA})_2$ vapour in the presence of water vapour decreases greatly the selectivity of film growth in comparison with the 'water-free' technique.^{171,205} On the other hand, the presence of water vapour increases the growth rate. In order to keep this advantage and still preserve the process selectivity, the films are prepared at rather high substrate temperatures in the absence of H_2 (He, Ar as carrier gases).^{171,190,226} If high selectivity of the process is required,

another variant is used in which such a substrate or barrier layer material is selected where water molecules are adsorbed poorly.²⁰⁵

Analysis of the dependence of the properties of the growing copper film, which is formed upon decomposition of $(\text{HFA})\text{Cu}(\text{VTMS})$ vapour, on the thickness of the primary copper layers on SiO_2 showed³⁹⁷ that the highest deposition rate of copper is observed at a copper layer thickness of 4 nm, and the lowest SER of the film is observed at a thickness of 15 nm. The selectivity of the CVD process with the use of this CCC in the Cu/SiO_2 system at temperatures below 200°C depends on the carrier gas and on the CCC vapour partial pressure.³⁰⁴

Awaya *et al.*²²⁹ conducted a comparative study of the effect of the β -diketone excess on the rate and selectivity of CVD of copper strips upon decomposition of $\text{Cu}(\text{HFA})_2$ and $(\text{HFA})\text{Cu}(\text{VTMS})$ vapour. The copper strips were deposited in the presence of water vapour on copper substrates with SiO_2 templates previously sputter-deposited on the surface, at a substrate temperature of 390°C . It was found that the optimum (fast and selective) process for the preparation of copper strips involves two stages. In the first stage, the substrate is treated with $\text{H}(\text{HFA})$ vapour in the presence of H_2 ; after that, $\text{Cu}(\text{HFA})_2$ is fed into the reactor and reduced on the substrate in the presence of H_2 . However, the presence of a free β -diketone in the stage of $\text{Cu}(\text{HFA})_2$ reduction results in the loss of selectivity.

In the case where $(\text{HFA})\text{Cu}(\text{VTMS})$ vapour is used in CVD processes, copper with a sputter-deposited SiO_2 template was also used as the substrate; the substrate temperature was $160\text{--}180^\circ\text{C}$. It was shown that, unlike in the experiment with the $\text{Cu}(\text{HFA})_2$ vapour described above, the presence of $\text{H}(\text{HFA})$ in the stage of strip formation increases the rate of filling the template channel; however, this completely suppresses the process selectivity, as distinct strip edges could not be obtained. It is believed²²⁹ that such a different behaviour of copper(I) and copper(II) compounds in this case is due to the difference between their decomposition mechanisms. Optimisation of the CVD process for film deposition with the use of vapour of copper(I) derivatives and similar templates was considered by Norman *et al.*³⁹⁸

Some increase in selectivity can be achieved by the preparation of copper strips on the same substrates, *viz.*, Cu/SiO_2 (template), from $(\text{HFA})\text{Cu}(\text{VTMS})$ vapour. This is due to the fact that adsorption of the precursor molecules on SiO_2 , which decreases selectivity, depends directly on the presence of reactive hydroxy groups on the substrate surface.^{386,399} Therefore, to exclude a decrease in selectivity, it was suggested³⁹⁹ to pre-treat the SiO_2 surface with dichlorodimethylsilane vapour. This compound eliminates the reactive OH groups from the SiO_2 surface, thus creating unfavourable conditions for adsorption and film growth at these sites. Nevertheless, as the overall process selectivity is controlled by several factors (*e.g.*, the substrate temperature and the dichlorodimethylsilane vapour pressure), it is difficult to obtain reproducible results.

The selective deposition of copper films can also be provided by using thermally grown SiO_2 as the substrate.^{400,401} In this case, the presence of H_2 during the process [which is usually the case for processes based on $\text{Cu}(\text{II})$ derivatives] is an unfavourable factor for the selectivity, as it results in reduction of the SiO_2 surface layer and generation of OH groups.⁴⁰²

A study of nucleation upon decomposition of $(\text{HFA})\text{Cu}(\text{VTMS})$ on a SiO_2 surface 'freed' from the OH groups showed that under these conditions, an increase in the flow rate of the starting CCC virtually does not affect selectivity;⁴⁰³ the pressure in the reactor becomes the main parameter for controlling selectivity.

$\text{Cu}(\text{HFA})(1,5\text{-COD})$ manifests certain selectivity with respect to the substrate material: the formation and growth of copper films on the surfaces of such dielectrics as SiO_2 and Si_3N_4 occurs with much greater difficulty than on metal substrates.³³⁴ However, this effect is not observed at sufficiently high temperatures ($> 200^\circ\text{C}$).³³⁰

A very high selectivity in the deposition of copper films in 'metal-SiO₂' systems is achieved if Cu(HFA)(PMe₃) and Cu(HFA)(PEt₃) complexes are used.³³¹

An unexpectedly high selectivity with respect to SiO₂ was shown by copper(I) pyrazolyl borate complexes as the starting CCC upon deposition on Pt/SiO₂, Au/SiO₂, Al/SiO₂ and W/SiO₂ substrates.³⁷² However, this effect was not observed on the Pd/SiO₂ substrate relative to SiO₂.

2. Use of substrates made of polymeric materials in CVD processes

The use of polymers as substrate materials in CVD processes has certain advantages. For example, it was found that the chemisorption of precursor molecules and the adhesion of copper films to polyimide substrates are much weaker than in the case of SiO₂; this fact enables highly selective deposition.⁴⁰⁴ CVD processes with the use of Teflon for the preparation of copper films have become especially popular.

Teflon is used as a dielectric layer with unique properties, such as high resistivity and small dielectric constant. When combined with the low SER of copper films, this affords a very promising basis for the creation of fast microelectronic devices with short signal delay times.⁴⁰⁵

In this case, selectivity is based on two processes. Laser irradiation of the Teflon surface results in cleavage of the polymer chains with simultaneous formation of cross-links between the chains and perfluorocarbons with short chains in the near-surface layer. Both of these processes result in a strong decrease in the copper adhesion on the irradiated substrate areas.⁴⁰⁶ Alkaline etching of Teflon results in partial defluorination of the surface layer to a depth of ≥ 300 nm and, hence, formation of a rough surface enriched with carbon atoms, which favours the efficient adhesion of copper films.^{405, 407} Hence, a combination of irradiated and etched zones on a Teflon surface can serve as a template owing to purely mechanical properties.

The principles of 'Teflon technologies' were formulated in a series of papers.^{408–410} The process usually includes three stages: alkaline etching, creation of a pattern by KrF laser radiation, and high-selectivity CVD of the film (the copper film remains only on the etched areas). In the best experiments, the deposition rate of up to $1 \mu\text{m min}^{-1}$ was reached and the SER of the films was $\sim 1.8 \mu\Omega \text{ cm}$.⁴¹⁰

VII. Conclusion

Until 1995 accumulation of basic experimental data and the accompanying development of concepts on the mechanisms of CVD of thin copper films with the use of volatile CCC had occurred. Subsequently, the research in this field reached a qualitatively different level.

Over the last two or three years, a certain decrease in the number of original papers was accompanied by an increase in the number of patents obtained both in the fields of the new volatile CCC, the ways for the synthesis of the already known compounds, and the specific details of CVD processes. This is also true for copper(I) and copper(II) derivatives as the starting CCC: the former are attractive due to the low temperatures of evaporation (sublimation) and decomposition on a substrate and the high film deposition rates; the latter, due to the stability during storage and the rather simple synthesis.

For example, copper(II) 6-ethyl-2,2-dimethyloctane-3,5-dionate was patented as a new starting volatile CCC.⁴¹¹ A series of patents were obtained for many compounds as potential starting CCC for CVD processes in the series of complexes of Cu(HFA) with silylalkenes^{412–415} and silylalkynes.⁴¹⁶ Analysis of the composition and properties of the compounds patented shows that by varying the electronic effects of the substituents at the silicon atom and in the diketone fragment, it is possible to reach an optimum ratio between the stability of the compound and its ability to decompose at low temperatures.

Let us note some technological patents with the use of (HFA)Cu(VTMS). A two-stage CVD process based on this CCC with addition of H(HFA) vapour⁴¹⁷ and H₂O vapour⁴¹⁸ has been patented. It should probably be expected that the number of patents in this field will increase.

Yet another trend worthy of note is the fast progress in the technologies for the selective deposition of films. The 'Teflon technologies' are a significant but not the only achievement in this field. The first specialised review devoted to these technologies⁴¹⁹ generalised the results obtained by that time. So far, a number of important studies have been completed (see, *e.g.*, Refs 420 and 421) that allow one to state that new microelectronic devices have been created using these technologies.

In our opinion, one more promising field for the application of CVD technologies based on volatile copper(II) and copper(I) compounds is the preparation of copper films doped with other metals within one technological process. For example, it was found that the doping of copper films with zirconium atoms provides a good protection against electromigration with an insignificant increase in SER.⁴²² The addition of a small amount of Pd(HFA)₂ to (HFA)Cu(VTMS) vapour results in a copper film containing $\sim 0.5\%$ Pd, which is completely stable against oxidation in air up to 300°C (see Refs 423 and 424). Attempts at synthesis of similar films doped with Co (see Refs 425 and 426) and Sn (see Ref. 427) were reported. Further development of studies in this field may well result in new materials with unique properties.

A conceptually similar approach is the development of CVD methods for the integrated deposition (using the same equipment) of a buffer layer onto a silicon substrate and a copper film atop this layer. The first study using this approach made it possible to obtain a copper film with very good characteristics (SER = $1.8 \mu\Omega \text{ cm}$) from (HFA)Cu(VTMS) vapour on silicon substrates with a TiN layer sputter-deposited prior to copper deposition.³⁸⁹

Perhaps, the above study reflects the most fundamental trend in the field, *i.e.*, the transition from separate experimental studies on the CVD preparation of copper films with the use of concrete starting volatile copper compounds to the creation of integrated CVD technologies with full optimisation of all the conditions of the process up to the preparation of the final product.

Spectacular examples of this approach include: the complete optimisation of a CVD process based on the industrially produced CCC of the CupraSelect grade ('Schumacher', Germany),⁴²⁸ the study where the technological approach to super-resolution resists was suggested,³⁹² and the study suggesting the full-scale CVD production of copper films with SER $< 2.0 \mu\Omega \text{ cm}$, deposition rate $> 200 \text{ nm min}^{-1}$, good adhesion and selectivity, and with ensured reproducibility of the properties of the batch films.³⁹⁰ It is obvious that the number of studies in this field will increase.

In addition, the CVD-based preparation of copper films can be a technological component of the production of more complex systems. Recently, a technique for optimal CVD of copper films as an intermediate stage in the production of absorbing layers for solar batteries based on CuInSe₂ was developed.⁴²⁹

Considerable help in the development of CVD technology for the deposition of copper films is provided by the database for quantum-chemical calculations that has appeared recently. For example, the deposition of copper films from (HFA)Cu(VTMS) vapour in a stream of argon was simulated numerically on a computer using the PHOENICS-CVD program and this database.⁴³⁰ The calculations made it possible to optimise both the conditions of the process and the equipment.

In conclusion of the topic of the development and creation of volatile copper(I) and copper(II) derivatives, it is necessary to mention the attempts to go from searches for new specific technologically promising substances to the development of a general methodology for the synthesis of starting volatile CCC, based both on the analysis of the crystal and molecular structures of the already existing CCC and on quantum-chemical calcula-

tions of the thermodynamic parameters of crystal–vapour phase transitions. Developments of suitable algorithms are under way,^{431,432} and it may well be that this approach has great prospects.

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